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Q1 Electrodeposited lead dioxide coatings**Q2 Xiaohong Li,^a Derek Pletcher^b and Frank C. Walsh^a**

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Lead dioxide coatings on inert substrates such as titanium and carbon now offer new opportunities for a material known for 150 years. It is now recognised that electrodeposition allows the preparation of stable coatings with different phase structures and a wide range of surface morphologies. In addition, substantial modification to the physical properties and catalytic activities of the coatings are possible through doping and the fabrication of nanostructured deposits or composites. In addition to applications as a cheap anode material in electrochemical technology, lead dioxide coatings provide unique possibilities for probing the dependence of catalytic activity on layer composition and structure (256 references).

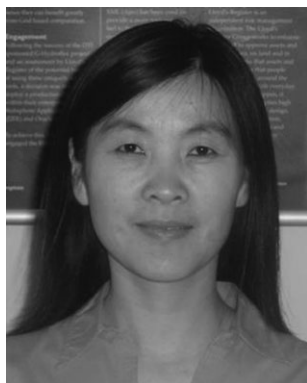
1. Introduction

Electrode coatings are now extensively employed to improve the performance of modern electrochemical technology.¹ Lead dioxide (PbO₂) is perhaps the grandfather of such coatings first investigated more than 150 years ago.² The earlier studies and applications were, however, limited to coatings formed *in situ* on lead or lead alloys and anodes of this type always

suffered from continuous corrosion of the underlying lead substrate. It is only much more recently that the preparation by electrodeposition of stable lead dioxide layers on inert substrates (typically titanium or carbon) has re-ignited interest in lead dioxide as an anode material. The reasons for this interest are clear. Lead dioxide coatings have a low cost compared to those based on precious metals, high electrical conductivity (comparable to metals), high oxygen overpotential and good stability in controlled conditions leading to possible application in new processes. In addition, from an academic viewpoint lead dioxide is a fascinating material. Lead dioxide coatings can be prepared with different phase structures, a wide range of surface morphologies and as both

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Derek Pletcher obtained his BSc and PhD in Chemistry from the University of Sheffield and has been a member of the Electrochemistry Group in Southampton since 1967 (presently, a Professor Emeritus). His research involving >200 co-workers has sought to build bridges between fundamental electrochemistry and electrochemical technology. These activities have resulted in >330 papers and >30 reviews. Derek Pletcher has been a consultant

to companies in Europe and North America, an organiser/presenter of short courses for academic and industrial audiences and an author including "A First Course in Electrode Processes" (RSC, 2009). He is a Fellow of US Electrochemical Society and has been awarded prizes including the Vittorio de Nora Prize (US Electrochem. Soc., 2010).

1 doped and undoped materials giving rise to significantly
different catalytic activities. In the long term, lead dioxide
can contribute substantially to a fundamental understanding
of the relationship between the coating structure and catalytic
5 activity, important to all fields of catalysis.

This review focuses on lead dioxide coatings, typically with
a thickness of 5–20 μm, formed *ex situ* by electrodeposition
onto inert substrates such as titanium or carbon from aqueous
electrolytes containing Pb(II). Those formed *in situ* on lead
10 metal or lead alloy anodes in media such as sulfuric acid where
an insoluble lead(II) compound is an intermediate in the
formation of the lead dioxide layer are only considered where
knowledge of their chemistry is helpful to the story of lead
dioxide layers on inert substrates. Discussion of the lead
15 dioxide electrode as met in the positive plate in the lead-acid
battery will be completely excluded; in this context, the
electrode consists of a thick layer of PbSO₄/PbO₂ paste, quite
different from the anode coatings considered here. Even so, it
should be recognised that the lead-acid battery is to be found
20 in all automobiles and is, perhaps, the battery most familiar to
the layman—it still represents some 40–45% of the sales value
of all batteries worth some \$15 billion to their manufacturers.
The interested reader is referred to a number of texts that
cover lead-acid battery technology.^{3–10}

25 Much of the recent literature addresses the twin goals of
developing lead dioxide coatings that allow high current
densities and efficiencies for particular electrode reactions
and enhanced stability of the coating. Long term stability is
always a critical issue when lead dioxide anodes are considered
30 because corrosion of the coating must lead to contamination
of the product/effluent with toxic lead(II). This review will
highlight the extensive literature of the past twenty years and
cover the chemistry and electrochemistry of lead dioxide layers
formed by electrodeposition, the influence of deposition con-
35 ditions on the structure and properties of the PbO₂ layers
including doped, composites and nanostructured layers. It will



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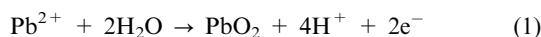
40 author of > 300 papers and 4 books, a willing participant in
short courses and an active consultant. He has been an Invited
Lecturer at International Conferences throughout the world and
received a number of awards, most recently election as a Fellow
of NACE International (the International Society focused on
55 corrosion).

also consider potential applications of such PbO₂ anodes. We
are not aware of any substantial reviews of lead dioxide
electrodes in recent years. The history and fundamental
chemistry of PbO₂ anodes is covered in 1972 and 1986 reviews
by Hampson,^{5,11} a 1979 book by Kuhn,⁸ a 1990 Chemical
5 Review of electrode materials¹² and a more recent chapter by
Salkind *et al.*¹⁰ The period since the last review has seen major
developments in lead dioxide coatings.

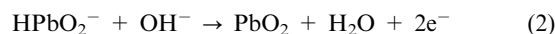
2. Basic electrochemistry

2.1 Thermodynamics

Lead dioxide may be electrodeposited onto inert substrates
such as titanium or carbon from a number of media where the
Pb(II) is soluble, *e.g.* nitric acid, perchloric acid, methane-
sulfonic acid, acetate buffer when the Pb(II) is present as Pb²⁺
or sodium/potassium hydroxide when the Pb(II) is present as
plumbite. In the acidic media the overall electrode reaction
may be written



and in the alkaline media



At 298 K, the equilibrium potential for the PbO₂/Pb(II) couple
is given by¹³

$$E_e(1) = 1.455 - 0.029 \log a_{\text{Pb}^{2+}} - 0.118 \text{ pH} \quad (3)$$

Fig. 1 shows the equilibrium potential plotted as a function
of pH for two concentrations of Pb(II) and the equilibrium
potential for the O₂/H₂O reaction as a function of pH. Three
conclusions are evident:

(i) In acid solution and on open circuit, lead dioxide is only
metastable since its dissolution by reaction with water to give
oxygen and Pb(II) is always thermodynamically favourable. In
media where the only Pb(II) in solution arises from corrosion
of the PbO₂ coating (as, for example, in any application of a
PbO₂ anode), lead dioxide will be metastable even in neutral

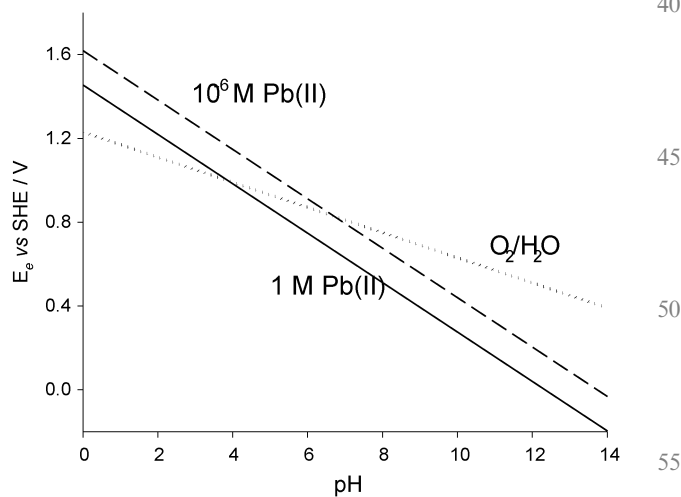


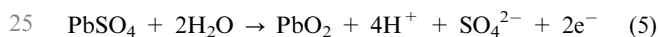
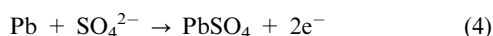
Fig. 1 The equilibrium potential plotted as a function of pH for two
concentrations of Pb(II) and the equilibrium potential for the O₂/H₂O
reaction as a function of pH.

1 solutions. Only in alkaline solutions will lead dioxide be
 2 thermodynamically stable. When employed in a practical
 3 electrolysis when the electrolyte may contain organics, halides
 4 or other species, the rate of corrosion will also need to consider
 5 oxidation of these species by lead dioxide (lead dioxide is, in
 6 fact, used as an oxidant in organic synthesis). All such
 7 oxidisable species will accelerate corrosion.

(ii) Lead dioxide electrodes can only be used in applications
 8 that require a rather positive potential. If a potential positive
 9 to the equilibrium potential is applied, the coating will be
 10 protected from corrosion. On the other hand, at any potential
 11 significantly negative to the equilibrium potential, cathodic
 12 reduction and dissolution of the lead dioxide coating are to be
 13 expected.

(iii) The substrate material must be stable to corrosion at the
 14 high positive potentials used both for the electrodeposition of
 15 the PbO_2 layer and the applications of the coated electrodes;
 16 pinholes and other faults in the coating are always possible
 17 and will lead to exposure of the substrate to the electrolyte
 18 with a consequent risk of substrate corrosion.

When a lead dioxide coating is formed *in situ* on a lead
 19 surface in sulfuric acid media, the anode reactions are:



and the equilibrium potentials are given by¹³

$$E_c(4) = -0.356 - 0.029 \log a_{\text{SO}_4^{2-}} \quad (6)$$

$$E_c(5) = 1.685 + 0.029 \log a_{\text{SO}_4^{2-}} - 0.118 \text{ pH} \quad (7)$$

Again it may be concluded that this layer is metastable on
 20 open-circuit in acid media because of reaction with water to
 21 give oxygen and except at very positive potentials that the
 22 layer will undergo cathodic reduction. In addition, however, it
 23 is clear that if any lead substrate is exposed to the sulfuric acid
 24 medium, there is a strong driving force for corrosion and
 25 perhaps the formation of a less conductive film *via* reaction (4).

Studies of $\alpha\text{-PbO}_2$ and $\beta\text{-PbO}_2$ would indicate that the phase
 26 has little influence on the thermodynamics of the reactions
 27 above, the equilibrium potentials differing by approximately
 28 10 mV.¹⁰ The $\beta\text{-PbO}_2$ phase is, however, thermodynamically
 29 the more stable phase.^{5,10}

2.2 Kinetics

Fig. 2 shows typical cyclic voltammetry for the deposition and
 30 dissolution of lead dioxide onto an inert substrate.¹⁴ The
 31 voltammograms were in fact recorded for a vitreous carbon
 32 disc electrode in a methanesulfonic acid solution and the 1st
 33 and 5th scans are shown but the voltammetry would be similar
 34 for other inert substrates and acid media. On the first scan
 35 with a clean vitreous carbon surface, deposition does not
 36 commence until close to the positive limit and the anodic
 37 current density is higher at the beginning of the reverse sweep.
 38 On the 5th scan, the deposition current density commences at
 39 substantially lower potential, say +1.63 V and the current
 40 densities are much larger and tending to a mass transport
 41 controlled plateau beyond +1.70 V. Reduction of the PbO_2
 42 layer back to Pb^{2+} is seen as a sharp symmetrical cathodic
 43 peak.

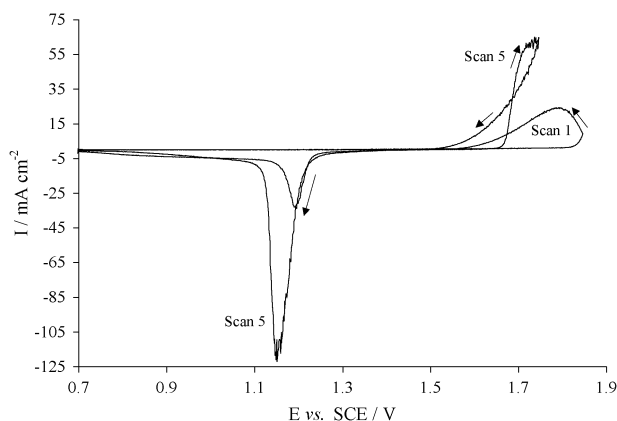


Fig. 2 Cyclic voltammograms recorded at a rotating vitreous carbon
 44 disc electrode ($\omega = 200 \text{ rpm}$) in a solution of lead(II) (300 mM) in
 45 aqueous methanesulfonic acid (2 M). The figure shows the first scan
 46 after polishing the vitreous carbon disc and the fifth during continuous
 47 cycling. Potential scan rate 50 mV s^{-1} . Temperature 298 K.¹⁴ Repro-
 48 duced by permission of The Royal Society of Chemistry.

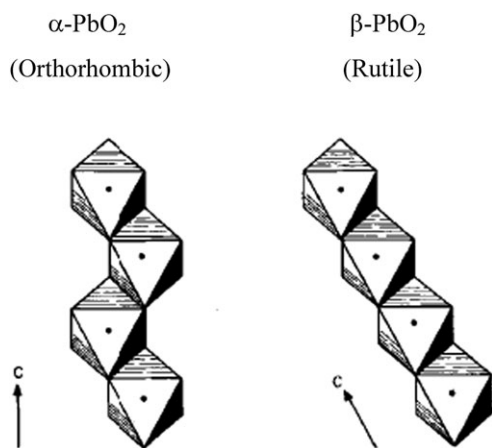
49 peak commencing about +1.20 V. With potential cycling, this
 50 peak grows as a thicker PbO_2 layer is deposited. All these
 51 features are typical of a deposition reaction involving nuclea-
 52 tion and growth of a phase on an electrode. Furthermore, the
 53 limiting current density towards the positive limit on the 5th
 54 cycle confirms that PbO_2 may be electrodeposited at a high
 55 rate. There is charge balance between deposition and dissolu-
 56 tion of the lead dioxide but even when a PbO_2 layer is present,
 57 the $\text{PbO}_2/\text{Pb}^{2+}$ couple is not electrochemically reversible—
 58 there is a potential range between +1.50 V and +1.20 V when
 59 almost no current is observed. But the clear conclusion is that
 60 a PbO_2 coating will not be stable negative to +1.20 V.

Voltammograms for the deposition and dissolution of PbO_2
 61 at most inert substrates and in many media are very similar to
 62 that shown in Fig. 2 and hence these conclusions are general
 63 for all media. Indeed the voltammetry of lead in sulfuric acid
 64 shows similarity as the formation of lead sulfate passivates the
 65 surface until conversion to lead dioxide occurs and reduction
 66 of lead dioxide back to lead sulfate gives a similar cathodic
 67 peak.^{5,15} It is interesting to note, however, that the kinetics of
 68 the $\text{PbO}_2/\text{PbSO}_4$ couple are significantly faster than the $\text{PbO}_2/$
 69 Pb^{2+} couple leading to lower overpotentials for both
 70 formation and reduction of PbO_2 .

The mechanisms for the formation and reduction of PbO_2
 71 are multistep and complex and remain the topic of study and
 72 speculation (see later). They will also depend on the system
 73 and conditions. Hence, it is not helpful to discuss quantitative
 74 kinetics. The voltammetry in Fig. 2, however, is a useful guide
 75 to the behaviour of lead dioxide layers in practice.

2.3 Phase composition and structure

Lead dioxide is polymorphic and the two modifications are
 76 well defined. $\alpha\text{-PbO}_2$ has the orthorhombic structure of
 77 columbite (space group $Pbcn$, V_h)¹⁴ and $\beta\text{-PbO}_2$ has the
 78 tetragonal, rutile structure (space group $P4/mmm$, D_{4h}^{14}).^{5,16}
 79 In both cases (Fig. 3), each lead(IV) ion is in the center of a
 80 distorted octahedron and the essential difference is in the way
 81 in which the octahedra are packed. In $\beta\text{-PbO}_2$, neighbouring

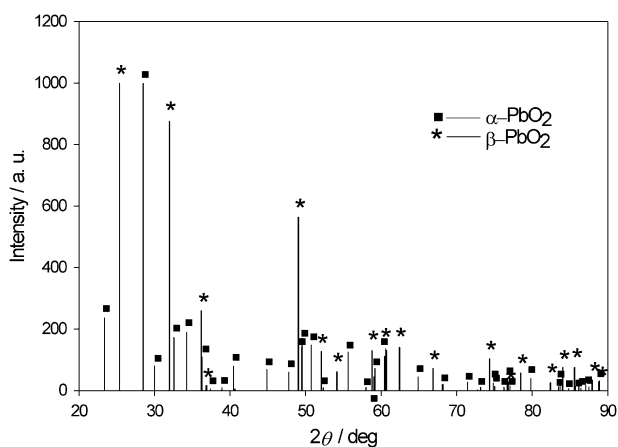


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Fig. 3 The structures of α -PbO₂ and β -PbO₂.¹⁶ The structures are based on the same oxygen octahedra but the octahedra are packed in a different way. Reproduced by permission of The Electrochemical Society.

20 octahedra share opposite edges, which results in the formation of linear chains of octahedra. Each chain is connected with the next one by sharing corners. In α -PbO₂, neighbouring octahedra share non-opposite edges in such a way that zig-zag chains are formed. Each chain is connected with the next one also by sharing corners.

25 α -PbO₂ and β -PbO₂ can be readily and qualitatively distinguished from each other using X-ray diffraction. Fig. 4 shows the standard powder diffraction patterns for the two phases.¹⁷ Strong diffraction peaks of both phases are present in the 2θ range 20°–40° and the peaks are clearly distinguishable. There can, however, be problems with the quantitative determination of the ratio of α -PbO₂/ β -PbO₂ phases due to a number of factors.^{5,18–22} Even so, Dodson²³ and Munichandraiah²⁴ proposed a method for estimating the relative amounts of α -PbO₂ and β -PbO₂ in mixtures of the two phases, which gave reproducible results within an error of 5%.

35 Moseley *et al.*²⁵ used high resolution transmission electron microscopy to investigate the real space structure of crystals of PbO₂ and explained the difficulties in refining the crystal structure of PbO₂ with the X-ray powder diffraction technique. A variety of crystal defects that had passed undetected by



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Fig. 4 Standard powder diffraction patterns recorded for samples of pure α - and β -phases of PbO₂.

1 conventional powder diffraction were revealed. α -PbO₂ with an apparently clean X-ray powder diffraction pattern was observed largely composed of crystals typified by extensive structural faulting. This faulting was manifest in an X-ray study only by a failure to achieve a satisfactory structural refinement. By contrast, a refinement of the β -PbO₂ structure converged well and the extent of crystal faulting appeared to have been much less. The recognition of this structural degree of freedom in PbO₂ is significant in view of its potential influence on properties such as electronic conductivity and electrochemical activity.

15 It is important to recognize that neither of the two modifications is fully stoichiometric and this is the reason for its high conductivity. The chemical compositions is correctly represented by PbO₂ - δ ·(xH₂O). The index “2 - δ ” indicates that there exists a variable deviation from the ideal stoichiometry, and the “xH₂O” states that a variable amount of water is dispersed through the PbO₂.^{6,26} Although this formula is convenient from the purely analytical point of view, it is somewhat misleading with regard to the crystallographic interpretation of non-stoichiometry. In fact, the anionic sublattice of the structure is known to be complete, and the dense packing of O²⁻ ions excludes the presence of “interstitial” H₂O or OH⁻. The deviation from stoichiometry is caused by structural disorder in the cationic sublattice. Rüetschi²⁷ proposed a detailed model where PbO₂ contains cation vacancies clustered together in layers which are acting as interfaces between crystallographically ordered regions. The cation vacancy layers may serve as hosts for Pb²⁺ ions. This model was able to describe the observed non-stoichiometry in a quantitative manner, in agreement with experimental results. Hence, the composition of PbO₂ was better written (Pb⁴⁺)_{1-x-y}(Pb²⁺)_y(O²⁻)_{2-4x-2y}(OH⁻)_{4x+2y}, whereby x designates the cation vacancy fraction and y the fraction of Pb²⁺ ions present, with respect to the total number of cationic sites.

2.4 Conductivity

40 Critical to its application as an electrode coating is the high conductivity of PbO₂. Mindt¹⁶ reports that the conductivities of α -PbO₂ and β -PbO₂ are close to 10³ ohm⁻¹ cm⁻¹ and 10⁴ ohm⁻¹ cm⁻¹, respectively, while studies of the Hall effect confirms that conduction results from the movement of electrons. It is widely considered that PbO₂ belongs to a group of n-type semiconductors and the conduction band in PbO₂ arises, to a first approximation, from the 6s levels of Pb⁴⁺ and the valence band from the 2p levels of O²⁻. Possible sources of free electrons in the PbO₂ include the deviation from stoichiometry discussed above, the incorporation of protons and the presence of impurities acting as dopants. Other workers suggest that β -PbO₂ is a metallic conductor. On the basis of self-consistent *ab initio* calculations of the electronic structure of β -PbO₂, Heinemann and co-workers²⁸ claimed that β -PbO₂ is a semimetal, with charge-carrier holes in an oxygen 2p band and electrons in a very broad strongly hybridized Pb 6s–O 2p band. Payne *et al.*^{29–31} studied the electronic structures of α -PbO and β -PbO₂ using X-ray photoemission, X-ray absorption and X-ray emission spectroscopies combined with band structure calculations. It is concluded that there is pronounced

1 hybridization between O 2p and Pb 6s and 6p valence states. The metallic nature of PbO₂ is shown to arise from occupation of conduction band states above the Fermi level of stoichiometric PbO₂, probably arising from oxygen vacancy defects.

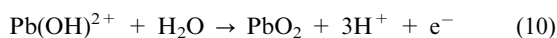
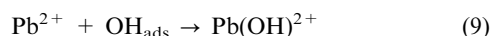
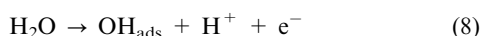
5 The conductivity of β-PbO₂ is comparable to metals such as Ti and Hg and higher than most forms of carbon. The lower value of conductivity for α-PbO₂ could result from several factors including (i) a smaller size of the crystallites in this modification, (ii) a higher carrier density in α-PbO₂, leading to a larger number of lattice defects where electrons are scattered, (iii) a high degree of orientation—the (100) axis is perpendicular to the substrate in α-PbO₂, (iv) anisotropy of the mobility in α-PbO₂, (v) the different crystalline structures of α-PbO₂ and β-PbO₂. Since the difference in the crystal structures results mainly from the different packing of octahedral of similar dimensions, large differences in the band structure and mobility are not expected.¹⁶

3. Deposition of lead dioxide

3.1 Nucleation and early growth

The analysis of chronoamperometric responses for the anodic deposition of PbO₂ onto platinum surfaces from perchloric acid, nitric acid, and acetate solutions was pivotal to the early development of the theories of nucleation and growth of conducting phases onto inert substrates by Fleischmann and coworkers.^{32–35} These studies led to the concepts of the nucleation of nanocentres of the new phase as the initial step, instantaneous and progressive nucleation, two and three dimensional growth, overlap of growing centres, thickening under electron or mass transfer control.³⁶ These studies of the early stages of electrochemical phase formation have been extended using other experimental techniques and to other solutions and substrates by several groups.^{8,37–42}

The sequence of chemical steps leading from Pb(II) in solution to solid lead dioxide has been the subject of much speculation. The most widely quoted mechanism is that proposed by Velichenco *et al.*^{43–46} involving adsorbed OH as a key intermediate:



although the experimental data do not allow easy distinction between possible mechanisms. Several papers using experiments such as a rotating ring-disc electrode have demonstrated that a soluble (or colloidal) lead(IV) intermediate is involved in both the formation and dissolution of lead dioxide^{47–51} and also the conversion of lead sulfate to lead dioxide.⁵² Again, however, it is uncertain whether the Pb(IV) species is a short lived intermediate in the major pathway or formed in a minor side reaction.

55 Ultrasound and microwaves have been shown to have a strong influence on the nucleation of lead dioxide at both vitreous carbon^{53–59} and boron doped diamond electrodes.^{60,61} This phenomenon can be associated with the reaction of OH• radicals (derived from aqueous sonolysis) with the carbon

surface and hence the enhancement of the number of active sites on the surface. Ultrasound and microwaves modify the morphology of the deposit as observed by SEM and can also improve the adherence of the deposit to the substrate.

3.2 Deposition of lead dioxide coatings

Many academic papers employ Pt, Au or glassy carbon as substrates for the deposition of lead dioxide. Clearly, this is unrealistic for any practical application. Titanium is the usual substrate for applications although an Indian group have promoted graphite^{62–70} and some papers have suggested tantalum⁷¹ and ebonex.^{72–74} Adhesion of the PbO₂ coating to titanium is, however, a problem. Certainly, the titanium, usually in the form of a plate or expanded metal mesh, must be pretreated before the anodic plating process^{8,75,76} in order to remove existing TiO₂ scale from the surface and roughen the surface and to prevent passivation. This pretreatment commonly involves, first sandblasting, then an alkaline degrease followed by etching in heated oxalic acid or hydrochloric acid for at least 30 minutes. Even this may be insufficient and various undercoats have been proposed—gold,⁷⁷ platinum,⁷⁸ tin dioxide,⁴⁷ TiO₂/Ta₂O₅⁷⁹ and TiO₂/RuO₂⁸⁰ are examples of such thin undercoats applied to titanium before deposition of the lead dioxide. Another approach has involved the use of multilayers of lead dioxide based materials with different compositions; the bottom layer is selected for good adherence and the top layer for the properties desired for the electrode reaction and/or stability to corrosion in the electrolysis medium. For example (a) Ueda *et al.*⁷⁹ recommend that the Ti is first coated with a thermally formed TiO₂/Ta₂O₅ undercoat, then a stress free α-PbO₂ layer and finally a β-PbO₂/Ta₂O₅ particle composite. (b) Feng and Johnson⁸¹ and Mohd and Pletcher⁸² recommend that doped PbO₂ coatings on Ti are prepared with an initial layer F⁻-doped material to give good adhesion and stability and a top layer of Bi- or Fe-doped lead dioxide to give the desired electrocatalytic activity. Graphite is also degreased and sometimes oxidised and roughened, either mechanically before deposition or, for example, by electroplating from a bath containing fine silica sand.⁶³

The literature on the electrochemical deposition of pure lead dioxide is very extensive. It is clear that the adhesion, surface morphology, ratio of α/β forms and catalytic activity can be influenced by many parameters including^{8,24,46,60,74,83–91}

- the substrate (Pt, Au, graphite, glassy carbon, Ti, Ti with undercoat, Ta).
- pre-treatment of the substrate surface.
- pH (1–6 or 13–14.5).
- anion of the electrolyte (nitrate, acetate, hydroxide, methanesulfonate, perchlorate).
- lead(II) concentration (1 mM–1 M).
- current density (1–100 mA cm⁻²), *i.e.* rate of deposition.
- potential for deposition, determining the rate of competing reactions, particularly O₂ evolution, as well as the rate of PbO₂ deposition.
- charge density, *i.e.* thickness of the deposit.
- temperature (190–363 K).
- mass transport regime in the plating bath (flow rate, rotation rate,^{14,55} and ultrasound).^{53–59,65}

1 Although many papers consider the influence of deposition
conditions on the quality of lead dioxide deposit, it is difficult
to draw general conclusions because of (a) the wide variety of
conditions and control parameters employed and the subtle
dependence of the form and properties of the coatings on the
deposition conditions, (b) not all the parameters are controlled
or stated in the papers, (c) the morphology and/or ratio of α/β
forms are stated without experimental data to support the
statement. For all these reasons it is difficult to compare results
from different laboratories, to draw definitive conclusions
about optimum conditions for deposition of a particular type
of deposit or to understand the correlation between type of
deposit and electrochemical properties.

This can be illustrated with one example. It is widely
believed that β -PbO₂ is deposited from low pH solutions and
 α -PbO₂ from higher pH solutions. However, when deposition
was carried out from 0.5 M Pb(CH₃SO₃)₂ + 0.5 M CH₃SO₃H
onto vitreous carbon,⁸⁹⁻⁹¹ the ratio of α/β forms was found to
be strongly dependent on temperature; pure α -PbO₂ was
formed at 298 K and pure β -PbO₂ at 348 K with both forms
deposited at intermediate temperatures. Also the low tempera-
ture deposit is compact and shiny and viewed with SEM is
smooth on a 10 μ m scale with crystallites with dimensions of
 \sim 50 μ m. In contrast, the β -PbO₂ deposit is rough by eye and
SEM reveals that it is made up of dense overlapping angular
crystallites of size $<$ 1 μ m. Such significant changes in struc-
ture for a change of temperature of 50 K emphasises the need
to control that parameter closely. In contrast, the variation in
the α/β ratio with current density or deposition charge was
small. In all papers concerning lead dioxide, it is critical that
all deposition conditions are fully stated and that the structure
of the layer is fully characterised.

Here, it will only be noted that a number of plating baths
giving high current efficiency for the formation of PbO₂ are
known and the conditions that lead to pure α -PbO₂ or pure
 β -PbO₂ deposits have been defined. For pure α -PbO₂, typical
conditions are:

(a) saturated lead acetate in 4 M NaOH, 298 K, $j =$
50 mA cm⁻² then 10 mA cm⁻²;

(b) 0.1 M lead acetate in 1 M sodium acetate, adjusted to
pH 5.5, 298 K, $j =$ 10 mA cm⁻²;

(c) 0.5 M lead methane sulfonate in 0.5 M methanesulfonic
acid, 298 K, $j =$ 50 mA cm⁻²;

(d) 0.1 M lead nitrate, pH 4.3, 298 K, $j =$ 3.5 mA cm⁻²; and
for pure β -PbO₂ typical conditions include:

(a) 1 M lead nitrate + 0.1 M copper nitrate (to avoid Pb
deposition and nitrate reduction on the cathode) in 1 M nitric
acid, 333 K, $j =$ 50 mA cm⁻² then 20 mA cm⁻²;

(b) 0.1 M lead nitrate in 1 M nitric acid, 333 K, $j =$
20 mA cm⁻²;

(c) 1 M lead methane sulfonate in 0.2 M methanesulfonic
acid, 333 K, $j =$ 50 mA cm⁻².

It is interesting to note that Velichenko and coworkers⁹²
recommend that, before use in an electrolysis, the potential of
the coating is cycled in sulfuric acid until a steady state
voltammogram is observed. It must be expected that the
PbO₂ structure will change during this potential cycling since
the potential range used involves the interconversion
PbO₂/PbSO₄. Indeed, the influence of potential cycling was

earlier investigated by Devilliers *et al.*⁷⁴ and it was shown the
voltammetry provides an approach to monitoring the changes.
SEM also clearly shows that the crystallite size decreases
substantially.

Even by eye, the deposits can have quite different appear-
ances. It is possible to deposit films with a highly reflective
black, metallic finish^{76,89-91,93} although more commonly they
have a grey or black matte appearance. When examined by
electron microscopy, the diversity of surface morphologies
becomes more apparent. Fig. 5 shows SEM images of lead
dioxide deposits. It can be seen that the deposits can be made
up of crystallites that are very flat, angular, rounded or
'cauliflower' like and their size is another variable. So far
there have been few systematic attempts to correlate the
structure as shown by SEM with the properties of the deposits.
Hyde *et al.*⁹⁴ used AFM to define a relationship between
deposition conditions and structure of deposits on B-doped
diamond and sought a correlation between reactivity and
structure using the oxidation of glucose as the model reaction.
AFM was also used to compare the surface morphologies of
deposits from methanesulfonic acid.⁹¹

Following the practices of metal plating, a number of
soluble additives have been used to enhance the properties
of lead dioxide layers, particularly to improve the adhesion

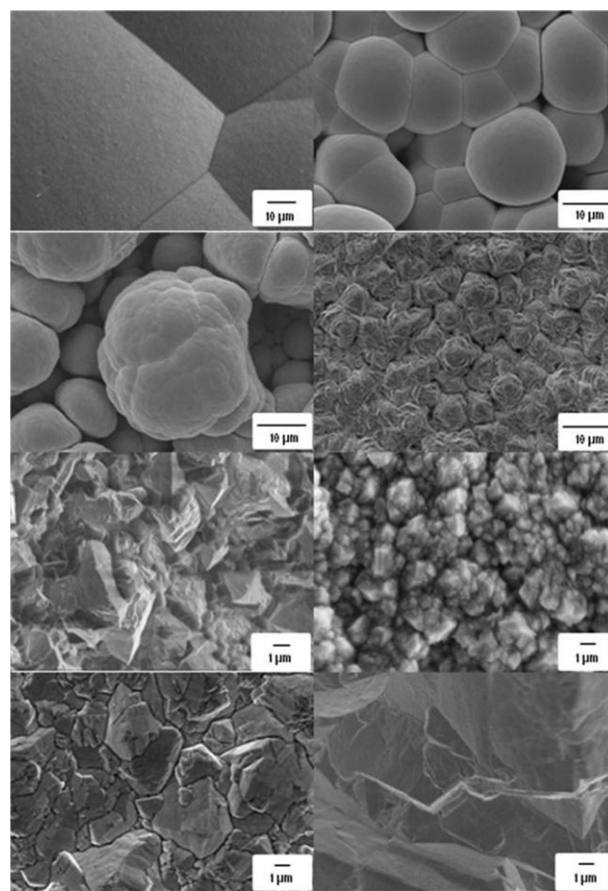


Fig. 5 SEM images of PbO₂ deposits with diverse morphologies. All these morphologies resulted from depositions carried out in Southampton using methanesulfonic acid electrolyte. Our thanks are due to Dr I. Sirés who supplied many of these images.

1 and control the stress. Such organic additives in acid nitrate
 baths have substantial effects on the PbO₂ layer: (a) Teepol⁹⁵
 was found to improve the adherence while creating a higher
 surface area, (b) triton X-100^{96,97} improved adhesion and
 mechanical strength while leading to higher overpotential for
 O₂ evolution, (c) gelatin and sodium dodecylsulfonate⁹⁷
 modified morphology and increased the α -PbO₂ content of
 the deposit, (d) polyvinyl pyridine⁹⁸ could be used to control
 both the morphology and crystal size. Other common additives
 are long chain, tetraalkylammonium ions⁹⁹ and these have
 found application in the soluble lead acid battery.^{89,100–107}

3.3 Doped lead dioxide

15 The past 20 years have seen much activity focused on the
 development of doped lead dioxide coatings with improved
 characteristics (*e.g.* catalytic activity, adhesion, stability).
 These doped lead dioxides are simply made by including an
 additional ion in the plating bath and there is no doubt that
 large improvements in performance are achieved. But again,
 the conditions used for the deposition of the doped materials
 are widely variable. The preparations have frequently involved
 the depositions from rather dilute solutions of Pb(II) and
 similar concentrations of the other ion and high levels of
 incorporation can be achieved; the ratio of M : Pb in the
 deposit can be > 1. In other laboratories, the concentration of
 the other ion is low and the deposit has a dopant level in the
 0.1–10% range. Should the former materials be considered as
 doped PbO₂ or mixed oxides where a major role of the lead
 dioxide may be as an inert, conducting matrix for a more
 active oxide? Certainly, in practice, highly doped materials
 have found greater application.

With each preparation, it needs to be defined whether the
 other ions are adsorbed, displace Pb(IV) from the lattice or
 whether the layer is a mixture of two oxides. Even the
 oxidation state of the dopant may be uncertain although it is
 commonly assumed that the elements are in their highest
 oxidation state. An early paper¹⁰⁸ concluded that at small
 dopant levels (100 ppm), the dopant ions increased the O/Pb
 ratio in both α -PbO₂ and β -PbO₂ and generally led to a
 decrease in the self-discharge rate. Structural studies using
 X-ray diffractometry of Bi-doped PbO₂ showed that the
 doping did not disturb the rutile structure of pure PbO₂ even
 when the Bi/Pb ratio reached 0.7 but there was evidence for an
 increased orientation of the lattice with respect to the substrate
 with increasing Bi content;¹⁰⁹ the average oxidation state of
 the Bi was estimated as +4.7. Amadelli and coworkers¹¹⁰ used
 SIMS and XPS to investigate the influence of F⁻ and metal
 ions on the PbO₂ films. The fluoride ion was found to be
 incorporated into the bulk structure and to decrease the extent
 of adsorbed water. In contrast, the cations (Fe(III), Co(II),
 Ni(II)) were not directly detected but were found to influence
 water accumulation; Fe(III) caused a decrease in OH⁻/H₂O
 adsorbed on the surface while Ni(II) had the opposite effect.
 More such studies are needed.

Table 1 summarises some of the dopants used and the
 specific improvements found. Fluoride ions and Fe(III) have
 been used effectively to improve the adhesion and the stability
 of lead dioxide anode coatings while several ions have been

Table 1 Doped lead dioxide anodes and the suggested roles for the dopants

Dopant	Purpose	References
Bi(III)	Catalyses oxidation of inorganic ions	81, 82, 109, 111–115, 119–123
	Catalyses removal TOC	
	Reduced fouling by organics	
Fe(III)	Catalyses organic oxidation and TOC removal, also cyanide oxidation	116, 117
	Enhances O ₃ evolution	111, 123
F(-)	Stabilises coating, improves adhesion	45, 88, 125
	Inhibits O ₂ evolution	126
As(III)	Oxidation of organics	120
Co(II)	Catalyses organic degradation	118
Ag(I)	Catalyses O ₂ evolution	127

demonstrated to catalyse the oxidation of both organic and
 inorganic species. Bi(III)- and Fe(III)-doped lead dioxides seem
 to be very general catalysts for oxidations.¹¹¹ Reactions of
 Bi(III)-PbO₂ reported include the oxidation of Cr(III) to
 Cr(IV),^{111–113} Mn(II) to Mn(III),^{111,114} cyanide,¹¹¹ thiophen
 derivatives^{111,114} and dimethyl sulfoxide.^{111,114} A number of
 these papers describe quantitative comparisons of the kinetics
 of oxidation at doped and undoped lead dioxide anodes;
 doping can lead to an increase in the rate of oxidation by a
 factor > 100 and, indeed, form a surface where reaction is
 minimal to one where the reaction is mass transfer controlled.
 Fig. 6 illustrates such catalysis using the example of cyanide
 ion oxidation at undoped and Fe-doped PbO₂.¹¹¹ At the
 undoped PbO₂, the cyanide is only oxidised at a very low rate.
 At the Fe-doped PbO₂, well formed oxidation waves are
 observed and the current at +1.4 V can be seen to be
 proportional to the square route of the rotation rate
 confirming that the oxidation is mass transfer controlled.
 The product from the oxidation of cyanide is cyanate.¹¹¹ In

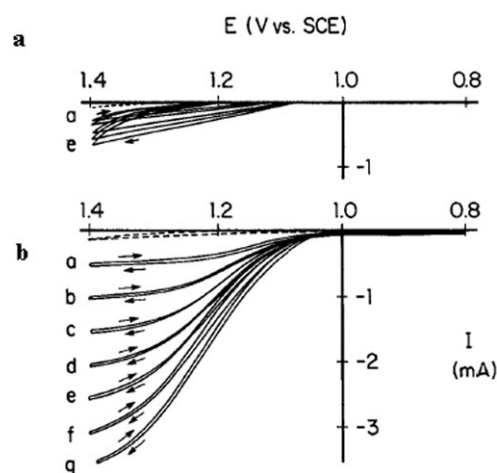


Fig. 6 Rotating disc voltammograms for the oxidation of 5 mM NaCN in aqueous NaHCO₃/Na₂CO₃, pH 10 at (a) undoped PbO₂ and (b) Fe-PbO₂ coatings on an Au rotating disc electrode. Rotation rates in revolutions per minute (a) 100, (b) 400, (c) 900, (d) 1600, (e) 2500, (f) 3600, (g) 4900. The dashed responses are for the electrolyte in the absence of NaCN.¹¹¹ Reproduced by permission of The Electro-synthesis Company Inc.

1 view of the high rates of oxidation of organics at some doped
coatings, it is not surprising that the studies have been
extended to the complete oxidation of organics and hence
for the removal of TOC/COD from effluent mimics.^{115–118}
5 Johnson and coworkers^{109,111,112,114–116,119,120,124,127} have
made detailed studies of the mechanisms for the enhancement
of rates by doping. They regard oxidations at lead dioxide
anodes as oxygen transfer reactions rather electron transfer
reactions and therefore stress the importance of the activation
10 of water as adsorbed OH radicals as the key step in the
oxidations. In addition, it was considered that pre-adsorption
of the molecule/ion to be oxidised may also be important. Low
additions of Bi (a Bi/Pb ratio <0.1) can be effective in
increasing the rate of oxidations¹⁰⁹ and similar enhancements
15 can be achieved by adsorption of the Bi onto a preformed
PbO₂ layer.¹²⁰ It is suggested that the Bi(v) sites promote the
formation of adsorbed OH radicals. In contrast, it is proposed
that the major influence of transition metals such as Fe(III) is
to enhance the adsorption of the organic molecule or inorganic
20 ion to be oxidised.¹¹¹ It cannot be ruled out, however, that
some metal ions, *e.g.* Fe(III), Ag(I), may catalyse oxidations by
undergoing a change in oxidation state. Finally, anion dopants
are considered to disrupt the structure of the PbO₂ lattice,
thereby enhancing the formation of adsorbed OH radicals.¹¹¹
25 The ability to tailor coating performance through doping
has also led to the fabrication of improved anodes with a
layered structure. The first layer is generally fluoride doped to
enhance adhesion and stability while the top layer is, for
example, Bi(III),⁸¹ Fe(III)¹¹⁷ or Co(II)¹¹⁸ doped to increase the
30 rate of oxidation.

3.4 Nano- and microstructured deposits

35 The fabrication of nanostructured materials has become an
important activity^{128,129} in modern research; in electrochem-
istry, the main objective has been to increase surface area and
hence the rate of reactions.

Two papers^{130,131} report the formation of PbO₂ nanowires
by electrodeposition into commercial anodic alumina mem-
40 branes with mean pore diameters of ~210 nm. The deposition
were carried out using a nitrate bath, with pH being used to
control whether α - or β -PbO₂ or α/β mixtures are formed.
After the deposition, the alumina membrane is dissolved in
sodium hydroxide to give free standing clusters of PbO₂
45 nanowires, see Fig. 7(a). Bartlett *et al.*¹³² describe deposition
of PbO₂ into self-assembled, close-packed arrays of poly-
styrene microspheres (diameters 500 nm or 750 nm), followed
by dissolution of the polystyrene microspheres with organic
solvent to give a highly regular structure that depends on the
50 thickness of the deposit compared to the diameter of the
microspheres. Fig. 7(b) shows a relatively thin layer where
deposition of PbO₂ stops before a monolayer of the poly-
styrene microspheres is covered while Fig. 7(c) shows the
foam-like deposit when deposition is carried out into multi-
55 layers of the microspheres.

The above papers describe highly ordered layer structures.
The potential advantage of a high area surface has led to other
approaches to modifying electrodeposited PbO₂ layers. The
strong dependence of surface morphology on the deposition

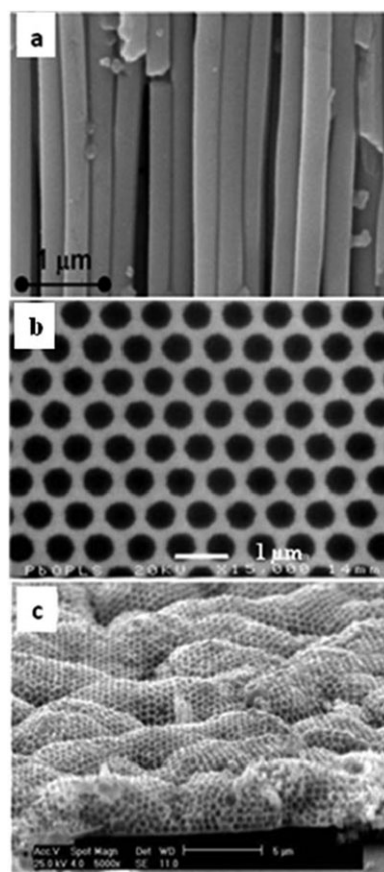


Fig. 7 SEM images of (a) β -PbO₂ nanowires deposited into an
alumina membrane after dissolution of the membrane.¹³⁰ Reproduced
by permission of The Electrochemical Society. (b) A macroporous
 α -PbO₂ film grown into a template consisting of a monolayer of
750 nm diameter polystyrene spheres after dissolution of the micro-
spheres.¹³² (c) A thick macroporous β -PbO₂ film deposited into a
30 template consisting of multilayers of 500 nm diameter polystyrene
spheres after dissolution of the microspheres.¹³² Reproduced by
35 permission of The Royal Society of Chemistry.

conditions was highlighted in Section 3.2 above and these
40 represent quite different areas of the PbO₂/solution interface.
Two approaches to the creation of high surface area
layers should be mentioned here. Blood *et al.*¹³³ describe
deposition from a high internal phase emulsion (HIPE); this
45 is an emulsion of the aqueous electrolyte containing Pb(II) with
a mixture of unsaturated organic compounds (precursors
to HIPE polymers). The lead dioxide layer formed by
electrodeposition from the HIPE was composed of
pyramidal features pitted with a large number of pores with
50 diameters in the range 0.5–2 μ m, see Fig. 8. In another
approach, Ghasemi *et al.*^{134,135} used pulsed current to create
featured surfaces.

In these papers, the focus was on increasing the charge
density of the positive electrode in lead acid batteries. This
seems a poor choice since the repeated PbO₂/PbSO₄ inter-
55 conversion makes probable the degradation of the nano-
structure. There must also be a concern about the stability
of very high area structures in contact with aqueous acids since
the rate of the PbO₂/water reaction must be increased.

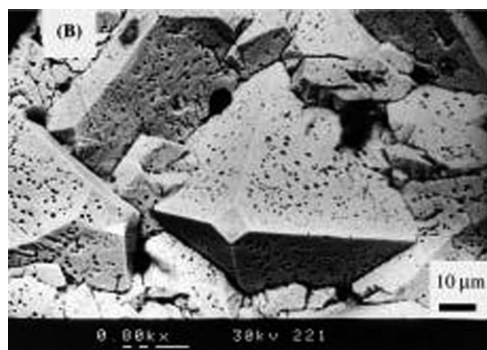


Fig. 8 SEM image of a PbO₂ electrode deposit produced at 3.2 mA cm⁻² for 21 600 s from a high internal phase emulsion on a carbon rod electrode substrate.¹³³ Reproduced by permission of Springer.

3.5 Composites

Composites are electrodeposits containing solid particles to introduce or enhance specific properties to the coating and are formed by deposition from baths containing dispersions of micro- or nano-sized particles and usually a surfactant. In general, composites in metal electroplates have been used to introduce/improve strength, wear resistance, corrosion resistance, self-lubrication, catalytic activity and other properties.^{136–138} A substantial number of lead dioxide composites have now been prepared and tested, see Table 2. The depositions are carried out in a variety of baths and with particulates with dimensions < 1 μm. The particulate content of the deposit initially increases with the particulate content of the plating bath but usually reaches a limit. It also depends on other control parameters such as current density and the mass transport regime.

Polymeric materials such as PTFE^{139–141} and polypyrrole¹⁴² were thought to introduce hydrophobicity and therefore both assist the release of gases and aid the interaction of organic molecules with the PbO₂ surface. The PTFE was also

Table 2 Lead dioxide composites—particulate constituents and the target property to be enhanced

Particulate added	Purpose	Reference
PTFE	Introduces hydrophobic character—lower η for O ₂ and oxidation of organics and improves stability.	139–141
Polypyrrole ^a	Introduces hydrophobic character—enhances oxidation of organics.	142
Al ₂ O ₃	Comparison with electroactive particulates.	149
RuO ₂	Catalysis of O ₂ evolution.	150
Co ₃ O ₄	Catalysis of O ₂ evolution.	143, 144, 146, 147
PbO ₂	Production of very rough lead dioxide anodes.	153
ZrO ₂	Erosion reduction.	159
TiO ₂	Photocatalysis.	92, 149, 155–158
Ta ₂ O ₅	Stable, high area electrodes.	79
IrO ₂ /Ta ₂ O ₅	Catalysis of O ₂ evolution.	152
CeO ₂	Stable coating Catalyses TOC reduction	160

^a Polypyrrole formed by electropolymerisation during deposition of PbO₂.

thought to reduce stress and thereby increase adhesion to the carbon substrate.

Musiani's group^{143–154} have sought to produce new electrocatalysts for the oxygen evolution reaction and other electrochemical oxidation processes essentially using the PbO₂ as a stable, conducting matrix to encapsulate particles that are more active catalysts for O₂ evolution and other reactions. They have studied composites with both electrocatalytic and inactive particulates and some particulates also enhanced the conductivity and/or mechanical strength of the PbO₂ matrix. Interestingly, co-deposition of conductive particles led to much rougher surface morphologies for the PbO₂ matrix while non-conducting particles, *e.g.* Al₂O₃ and TiO₂, did not influence its morphology.¹⁴⁹ Rough anodes could also be produced using PbO₂ particulates in a PbO₂ matrix.¹⁵³ The roughness is, of course, a favorable feature for electrocatalysis.

Co₃O₄ was the preferred particulate for O₂ evolution. PbO₂/Co₃O₄ composite electrodes exhibit much lower overpotentials and Tafel slopes^{143,147} in both acidic and basic media compared to pure PbO₂. Prolonged electrolysis tests confirmed good stability of the composites (no degradation was observed at room temperature during several weeks at an imposed current density of 100 mA cm⁻²), although a weakness of these composites was the tendency to undergo detachment from the underlying substrate when submitted to electrolysis at high temperature.^{144,145} PbO₂ was also shown to be a superior matrix than Pb or Ni for the Co₃O₄.¹⁴⁶ PbO₂/RuO₂ composite electrodes also exhibited catalytic activity for oxygen evolution reaction, in fact comparable to that of thermally prepared Ti/RuO₂ electrodes.^{150,151} In practice, however, in acid, reduction of the PbO₂ to give Pb²⁺ in solution or an insoluble salt (depending on the acid) occurred at the potential for O₂ evolution and the composite was also subject to open circuit corrosion. PbO₂/IrO₂/Ta₂O₅ composites were more stable but gave a higher overpotential for O₂ evolution.¹⁵²

Recently, the PbO₂/TiO₂ composites have attracted considerable attention due to their potential application in photoelectrocatalytic oxidation of organics in wastewater.^{92,155–158} Qu *et al.*^{155,156} reported the electrochemically assisted photocatalytic degradation of Acid Orange 7 and an azo-dye Orange II using the PbO₂/TiO₂ composite electrodes. The degradation efficiencies improved slightly with the TiO₂ content and with increase in potential. Jin *et al.*¹⁵⁷ utilized the PbO₂/TiO₂ composite electrode as an amperometric sensor to determine the chemical oxygen demand of waste waters. The method had a low detection limit and wide application range and the COD values compared well with determinations by a traditional method. Velichenko *et al.*^{92,158} examined the mechanism of PbO₂ electrodeposition in the presence of colloidal suspension of small TiO₂ nanoparticles, mean diameter of 5 nm. They concluded: (i) addition of TiO₂ nanoparticles to the electrolyte leads to enhancement of the rate of PbO₂; (ii) the mechanism is essentially the same as observed in the absence of TiO₂; (iii) the key aspect in this mechanism is the role of OH• radicals formed from the discharge of water; (iv) the service life of the composite during the photo-electrocatalytic oxidation of oxalic acid and benzyl alcohol was a factor of ~3 longer than traditional PbO₂ anodes.

4. Applications

Lead dioxide anodes based on both lead/lead alloy substrates and inert substrates, particularly carbon and titanium, have found diverse applications. The former are generally formed *in situ* in the process conditions when the electrolyte for the process contains an anion leading to an insoluble and 'protective' Pb(II) layer on the lead surface. As with the plated layers, the PbO₂ may be α - or β -phase or mixtures of the two depending on the oxidation conditions.¹⁶¹ On inert substrates, β -lead dioxide anodes are available from a number of suppliers worldwide but, commonly, literature reports employ 'home manufactured' coatings. Both approaches lead to uncertainties in interpreting and comparing results. As discussed in the previous section, the form (and presumably performance), including the lifetime, of lead dioxide coatings depends strongly on the deposition conditions; the conditions for the fabrication of the commercial coated anodes are never specified while the academic community have used a variety of preparative conditions (and some papers do not always fully specify them). In all applications, the use of lead dioxide anodes is dependent on a demonstration that the 'electrolyte' is not significantly contaminated by lead(II); the stability of the lead dioxide coating may be dependent on the nature and concentration of all components in the medium as well as the fabrication procedure and operating parameters.

4.1 Oxygen evolution as a counter electrode reaction

Lead dioxide anodes formed *in situ* in sulfuric acid on lead/lead alloy substrates have been widely used as oxygen evolving counter electrodes for processes employing a sulfuric acid electrolyte free of halide ions.^{1,8,162} The biggest application is the electrowinning of copper although similar technology is used for other metals such as zinc, nickel and chromium.¹ The technology is simple and designed to permit easy removal of the metal after deposition on the cathode. The metals are refined in open tank cells with parallel, alternate lines of cathode and anode plates; for copper, the tanks are similar in size to a swimming pool and each anode plate is a fraction of a square metre. The anode current density is generally in the range 10–100 mA cm⁻². The anode material is a lead alloy with 6–15% Sb and 0–1% Ag. The antimony hardens the alloy and improves its mechanical properties while the silver reduces the overpotential for oxygen evolution and hence the energy consumption for the process. In the process operating conditions, the anodes have an easily seen corrosion coating but with careful handling have a lifetime of several years. For the past 30 years, these lead anodes have received competition from DSA coatings (Ti/IrO₂ based dimensionally stable anodes), but the low cost and acceptable performance of the lead dioxide leads to their retention in many plants.

Another process that used a PbAg alloy anode in a sulfuric acid anolyte was the first version of the Monsanto process for the hydrodimerisation of acrylonitrile to adiponitrile.¹ This process employed divided, parallel plate cells in a bipolar stack. The catholyte was a complex mixture of organics and a proton permeable membrane was used to separate it from the anolyte and hence maintain a clean sulfuric acid anolyte. In these conditions, the lead dioxide anodes could maintain a

current density of 450 mA cm⁻². For reasons unassociated with the lead alloy anodes, in the 1980s this technology was modified to allow operation with an undivided cell and the anodes are now steel.

4.2 The manufacture of chemicals

Lead dioxide anodes have been extensively employed in the manufacture of peracids, their salts and strong oxidising agents and, in many cases, electrolysis is the only route for their manufacture. All such processes require high positive potentials and the only alternative anode material is the expensive Pt/Ti.

Over the past 50 years, perchlorates have been manufactured by the anodic oxidation of the corresponding chlorate and plants in the USA, Japan, Europe and India have used PbO₂ coated graphite or titanium anodes,^{8,12,62–70,162–164} the most detailed discussion of process conditions come from the Indian group led by Udupa.^{62–67} Typical conditions are an electrolyte consisting of 250 g litre⁻¹ of the chlorate, pH 7, at a temperature of ~330 K, a PbO₂ anode and a steel cathode and a current density of 50 mA cm⁻². The current efficiency is >80% with an energy consumption of 6.0–6.5 kWh kg⁻¹ of the perchlorate. Similar technology for the production of periodate has been described⁶² and processes have also been described for the formation of bromate¹⁶⁵ and iodate⁶² from bromide and iodide, respectively.

Lead dioxide anodes have also been used for the production of strong oxidising agents such as dichromate,^{78,111–113,166–168} manganese (III)^{109,114,119,169,170} and cerium(IV).^{169–172} Most commonly, these processes are used to regenerate the spent oxidising agent from the oxidation of organic compounds (*e.g.* anthracene, naphthalene, montan wax), etchants and polishing/plating baths and are therefore operated on a wide variety of scales. Technology based on parallel plate, membrane cells is now common and both lead and inert substrate based anodes have been employed. For example, the plant for the regeneration of chromic acid used for the conversion of anthracene to anthraquinone¹⁶⁸ required the regeneration of chromic acid by the oxidation of Cr(III) in a medium containing ~40–150 g litre⁻¹ of Cr(III) in sulfuric acid. The cells used 1 m² bipolar electrodes with lead anode and steel cathode surfaces and these were arranged in a bipolar stack of 39 cells with Nafion™ membrane separators. The current density was 150 mA cm⁻² and although anode corrosion occurred, the use of lead anodes several millimetres thick allowed continuous operation for several years. For the regeneration of chromic acid there are probably no alternatives to PbO₂ as the anode material. Pletcher and Tait¹⁶⁷ investigated the influence of the lead surface oxidation on the kinetics of Cr(III) oxidation.

For an extended period, the Miles Chemical Co in the USA ran a 45 ton year⁻¹ plant for the manufacture of dialdehyde starch with integrated electrolytic regeneration of periodate.¹⁷³ The technology employed PbO₂ anodes.

4.3 The generation of ozone

Ozone is an environmentally friendly oxidant with applications in the purification and sterilization of water, paper

1 bleaching, oxidation, deodorization, and decolorization of
waste water.^{174,175} It has, however, a very short half life and
must be generated on site at the time of use. The conventional
way to produce ozone is based on cold corona discharge
5 (CCD) technology where dry oxygen or air is flowed past an
electric discharge, producing a 2–3% concentration of ozone
in air. The overall energy consumption of the CCD process is
high because cooling and drying of air are needed in addition
to a high voltage discharge. Electrochemical ozone generation
10 has considered as an attractive alternative since the
1970s.^{124,126,176–202} Compared to the CCD technology,
electrochemical ozone generation has several advantages; for
example it can produce a higher *in situ* ozone concentration
without by-product and secondary pollution.

15 The electrolytic production of ozone requires a high positive
potential (the formal potential for the O₃/H₂O couple is
+1510 mV) and it is always produced alongside copious
oxygen evolution. Hence, the current efficiency is the major
factor determining energy consumption and inhibition of O₂ is
20 clearly an advantage. The anodic generation of ozone at lead
dioxide anodes has been reported in several aqueous media
including neutral sodium sulfate,¹⁷⁶ perchloric acid,^{178,179}
phosphoric acid,^{177,182} neutral phosphate,¹⁸⁰ sulfuric acid,¹⁸²
and fluoroboric acid;¹⁸² the current efficiencies vary in the
25 range 3–18%. The electrolyses are run at high current
densities, 600–1200 mA cm⁻² and the current efficiencies are
higher in acids at lower temperatures. It has also been reported
that the addition of fluoride or anions containing fluoride to
the electrolyte improves the current efficiency.^{124,182,186,192–194}
30 and β-PbO₂ doped with Fe or F also perform better than
undoped PbO₂.^{124,195} Because of the very positive potentials
essential to ozone generation, the only alternatives to lead
dioxide is vitreous carbon and diamond. Yields as high as 45%
have been reported for vitreous carbon in 62 wt% HBF₄ at
35 low temperatures^{181–184} but lead dioxide is more flexible in cell
design and the low cost choice.

Da Silva *et al.*^{196–200} emphasize that in addition to the
composition of the PbO₂ used for ozone generation, the
electrode morphology (*e.g.* porosity, roughness) also strongly
40 influences ozone generation kinetics and current efficiency. In
the case of more compact coatings the fluoroanions cause a
substantial effect on the current efficiency of ozone over the
complete current interval investigated while with less compact
coatings the influence of the fluoroanions is mainly verified at
45 current density less than 0.3 A cm⁻². This result emphasizes
the need for a detailed investigation of the electrode prepara-
tion parameters in order to optimise current efficiency and
reach a better understanding of the fundamental aspects
involved. Foller and Tobias¹⁸² also mentioned that different
50 PbO₂ surfaces can show remarkable variation in ozone yield
and found it necessary to chemically etch PbO₂ electrodes with
hydrogen peroxide and acetic acid before each use in order to
obtain reproducible results.

A significant advance in electrolytic ozone generation tech-
55 nology was accomplished by Stucki and co-workers.^{188–192}
They developed a novel, zero gap electrolytic ozone generator
using a solid, proton conducting polymer electrolyte
(Nafion[®]) and a PbO₂ anode and this has now been marketed
for over 20 years under the tradename Membrel[®]. It is

designed for the disinfection and purification of water and
1 hence to supply ultra pure water to, for example, the pharma-
ceuticals, fine chemicals, electronics and the food supply
industries. The core to the system is an electrolytic cell where
the 30 cm² electrodes are pressed up against the Nafion[®]
5 membrane to form an ‘MEA type’ structure. The anode
material is porous, sintered titanium coated with PbO₂ and
the cathode is a porous stainless steel structure coated with Pt.
This zero gap configuration improves the stability of the PbO₂
anode (by preventing erosion from solution flow and by
10 avoiding pH gradients at the electrode surfaces that would
result from the high operating current density in liquid
electrolytes) and allows water (with no added electrolyte) to
be fed to the back of the anode and electrolyzed to produce a
mixture of O₂ and O₃ on the backside of the anode and H₂ on
15 the cathode. In a high pressure format, the ozone exits the cell
as a highly concentrated solution of ozone, > 100 mg litre⁻¹;
otherwise it leaves as a gas. The cell is operated at a current
density of 0.5–2 A cm⁻² with a cell voltage of 3–5 V. This gives
a current efficiency of ~20% and an energy consumption of
20 65 Wh g⁻¹. Membrel[®] is marketed in units capable of
delivering 1 g hour⁻¹, 3 g hour⁻¹ or 9 g hour⁻¹ of ozone
and the units are said to operate continuously for over 3 years
without major maintenance.

Onda *et al.*²⁰¹ also operated a solid polymer electrolyte
25 electrolysis cell but used an anode structure with several layers
of PbO₂ coated titanium mesh with different mesh dimensions.
The finest mesh was placed against the membrane. The
authors claim that this cell design produces exit water with a
Pb(II) content more than a factor of 100 below the allowable
30 level for drinking water. Hence, this modified design can be
used for the sterilization of drinking water.

Ozone electrogenerated at PbO₂ has been shown to be effective
for the destruction of a wide range of organics including *trans*-
3,4-dihydroxycinnamic acid,²⁰² phenols,¹⁹⁵ reactive dyes.²⁰⁰
35 Amadelli and coworkers²⁰² suggest that the most effective way
to use the ozone is to feed it to a hydrogen peroxide forming
cathode since this generates a very high concentration of free
radicals. The ozone output also kills many germs, *etc.*

4.4 Water and effluent treatment

With increasing social and legislative pressures to ensure that
effluents are fully treated before discharge into rivers, lakes or
the sea, there have been extensive studies of the electrolytic
45 mineralisation of organic compounds with a particular focus
on compounds that are toxic or resistant to biological
treatments.^{111,203–206} It is widely believed that complete
mineralisation occurs by mechanisms dominated by oxygen
transfer and adsorbed or free OH radicals rather than direct
50 electron transfer from the organics to the anode.^{71,207,208} This
requires anodes that are stable at very positive potentials; lead
dioxide and B-doped diamond have proved the most suitable
materials. In general, B-doped diamond gives the highest rate
of mineralisation but such anodes are expensive and
55 doubts remain about their long term stability. This presents
opportunities for lead dioxide. Particularly in water and
effluent treatment, the absence of Pb(II) contamination of the
medium must clearly be demonstrated.

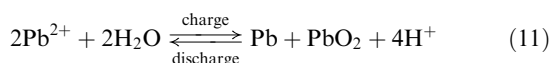
1 There have been many studies of the mechanisms for the
 degradation of organics at lead dioxide anodes using
 electrochemical, spectroscopic and intermediate product
 identification.^{71,88,111,203–215} The most compelling evidence
 5 for a role for OH radicals comes from the use of spin trapping
 agents^{88,209–212} but many of the steps in the complex reaction
 sequences remain speculation. There is also good evidence that
 doping the electrodeposited PbO₂ layer with elements such as
 Bi(III), Fe(III) and F⁻ accelerates oxidation, leads to more
 10 complete mineralisation and/or enhances the stability of the
 coating.^{81,86,117,121–126,216–222} It has also been reported that
 there are distinct differences in the performance of α- and
 β-PbO₂²²³ and morphologies²²⁴ of the lead dioxide surfaces.

The degradation of a large number of organic pollutants has
 15 been reported. These include phenol,^{71,118,121,122,216,217,222–232}
 aniline,²³³ benzoquinone,^{116,218} chlorinated phenols,^{87,219–221}
 nitrophenol,^{86,222,234,235} naphthol,²³⁶ glucose,^{237,238} oxalic
 acid,^{239,240} chloranilic acid,²⁴¹ indoles,²⁴² tannic acid,²⁴³
 1,2-dichloroethane,²⁴⁴ cresols,²⁴⁵ herbicides,^{246,247} pesticides,²⁴⁸
 20 surfactants²⁴⁹ and dyes.^{82,117,250,251} Substantial diminution of
 COD/TOC is generally possible with an acceptable current
 efficiency. Such studies, however, generally use electrolytes
 and pH conditions seldom found in real effluents and are
 satisfied with low current densities that would be unacceptable
 25 to industrial practice. The lead dioxide anodes need to be
 incorporated into realistic cell designs in order to give
 acceptable rates of mineralisation and to examine anode life-
 times with the real process streams in operating conditions.

Far fewer papers have considered the treatment of real
 30 effluents. Examples would include urine biomass,²⁵² landfill
 leachate,^{253–255} tannery waste,²⁴³ waste water,^{122,237} phenol
 streams,^{121,122} dye plant effluents¹¹⁷ and herbicide manu-
 facture effluents.^{246,247} Good levels of COD/TOC removal
 have been achieved although generally with rather poor
 35 current efficiency. In most cases, however, these effluents also
 contain chloride and this broadens the possible chemistry of
 the degradations with likely roles for chlorine, hypochlorous
 acid, *etc.* and hence to mechanisms not normally discussed in
 the academic literature.

4.5 The soluble lead(II) acid flow battery

A group in Southampton have been developing a novel flow
 battery intended for large scale energy storage.^{14,89,100–107,256}
 The overall cell chemistry is



and the electrolyte is methanesulfonic acid in which Pb(II) is
 50 highly soluble. The advantage of the system is that it requires
 only a single electrolyte and hence no membrane. Unlike other
 flow batteries the energy is stored as deposits on the two
 electrodes. Hence, the battery requires the electrodeposition
 and cathodic dissolution of thick layers of lead dioxide at the
 55 positive electrode (as well as thick layers of lead metal at the
 negative electrode). In some conditions it is possible to deposit
 thick and uniform lead dioxide layers from the methanesulfonic
 acid medium at quite high rates, see Fig. 9 and this can be
 discharged with good current efficiency. Indeed, it is possible

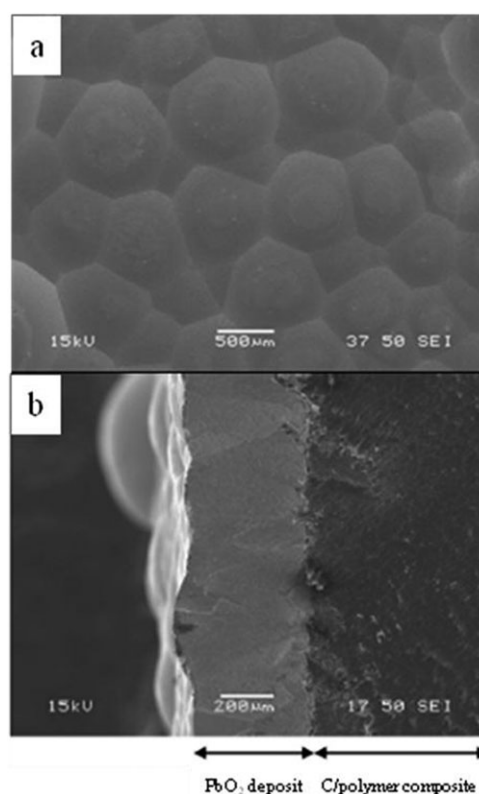


Fig. 9 SEM images of (a) the surface and (b) a cross section of a thick PbO₂ deposit grown from a solution of 0.5 M Pb(CH₃SO₃)₂ + 0.3 M CH₃SO₃H + 5 mM C₁₆H₃₃(CH₃)₃N⁺ at 50 mA cm⁻² at 298 K on a carbon polymer composite electrode.²⁵⁶ Reproduced by permission of The Electrochemical Society.

to cycle the battery more than 100 times with an energy
 efficiency of ~70% but failure eventually occurs led by
 incomplete dissolution of the lead dioxide. This incomplete
 35 dissolution is probably associated with an increase in pH
 within the pores of thick layers of lead dioxide. The preferred
 form of the lead dioxide is α-PbO₂; only α-PbO₂ is formed
 during the initial charge periods but, on continuous cycling,
 eventually a mixture of α- and β-PbO₂ is deposited and this
 40 may contribute to failure. While the battery has been scaled up
 to a 100 W bipolar unit, future work will focus on further
 improving the performance of the lead dioxide electrode and
 ensuring 100% current efficiency for the dissolution of the lead
 dioxide at the positive electrode.

5. Conclusions

Lead dioxide coatings on titanium or carbon now offer a
 cheap alternative to precious metal anodes for a number of
 50 applications and provided they are used in controlled condi-
 tions, such coatings can have extended lifetimes with no
 significant contamination of the cell effluent by soluble lead
 species. Electrodes with lead dioxide coatings already have
 applications in the manufacture of chemicals as well as water
 55 and effluent treatment and such applications are likely to
 expand.

Electrodeposition allows the fabrication of a family of lead
 dioxide layers with different physical and catalytic properties.

1 The conditions for the deposition of pure α -PbO₂, pure β -PbO₂ or mixtures of the phases are well established and it is possible to plate layers with very different surface morphologies and surface areas. In addition, the ability to deposit
5 layers with very different dopants and doping levels, nanostructured layers and composites greatly expands the possibilities. It is possible to tailor both physical properties such as appearance, adhesion, stress and conductivity and chemical properties, particularly the rate of anode reactions. Particularly
10 doping can have a large influence on electrode performance, introducing both greater stability and dramatically increasing catalytic activity. In some cases, oxidations that do not occur at undoped PbO₂ will become mass transport controlled with appropriate doping.

15 As yet the literature is weak in closing the links between the deposition procedure and the structure/morphology of the lead dioxide layer as well as between this structure and electrode performance, particularly the catalytic activity and the stability of the lead dioxide surfaces. On the other hand,
20 fundamental studies of lead dioxide coatings provide a new, and perhaps unique, avenue to understanding the relationship between the composition and structure of electrocatalysts and their activity. The diversity of PbO₂ layers that can easily be electrodeposited is unparalleled with other materials. The
25 requirement is for more careful characterisation of composition, structure, morphology and surface area and correlation with electrode performance.

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