Lead dioxide electrodes for high potential anodic processes[*]

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Doping of PbO_2 by cations (Fe^{3+}, Co^{2+} and Ni^{2+}), by F^- and by cations and F^- simultaneously is discussed as a way of improving the stability and electrochemical activity in processes occurring at high potentials. Doping allows the control of the amount of structural water in an oxide. Radiotracer experiments showed that high electrodeposition current densities favour the segregation of incorporated tritium (protons) at the surface. On the other hand, fluorine doping results in a marked decrease in the amount of surface oxygen species. The influence of doping with metal cations strongly depends on the nature of the metal. Iron behaves like fluorine, while nickel causes an accumulation of surface oxygen species. Doped PbO_2 electrodes have quite good activities for the electrogeneration of ozone. In particular, Fe and Co doped PbO_2 showed a current efficiency of 15–20 % for this process. This result is relevant to our recent studies on *"cathodic oxidation"*, *i.e.,* an ozone mediated electrochemical method in which an O_2 stream is used to sweep the O_2/O_3 gas mixture produced at a PbO_2 anode into the cathodic compartment of the same electrochemical cell containing polluting species.

Keywords: lead dioxide anodes, doping, ozone electrogeneration.

INTRODUCTION

Electrode materials with a good activity and stability at high potentials are interesting because of the electrochemical synthesis of important oxidants used in the chemical industry, such as perchlorate, peroxysulphate and ozone, and in studies on the abatement of recalcitrant pollutants by electrochemical methods.

Lead dioxide electrodes are still widely used for these purposes as the material is cheap and relatively stable under the high positive potentials required. The electrocatalytic activity of PbO_2 electrodes, as well as their stability, can often be considerably enhanced by the incorporation of some foreign ions added to the electrodeposition solution. Among these, Bi^{3+}, Fe^{3+}, Co^{2+} and F^{-},[1,2] gave very good PbO_2 electrodes for oxygen transfer reactions, including O_3 formation. Heavy doping would lead eventually

[*] Dedicated to Professor Dragutin M. Dražić in recognition of his contribution to electrochemistry.

to the formation of composite oxide materials. Both the low doping and mixed oxide approaches have some merit. In the first case, it is a way to maintain the high corrosion resistance of PbO_2 matrix and at the same time increase the electrocatalytic acitivity.

One mayor goal of the doping process is to tune the properties of the resulting oxide to some particular electrocatalytic process; interest may be focused, for example, on the control of surface hydroxyl-radicals through hindering or promoting water discharge. In this respect, understanding the details of the electrodeposition process is a key step for the preparation of oxide deposits possessing specific features for use in electrocatalytic processes. In this work, a brief account of our ongoing research in this field of study is presented with particular attention being paid to the case of doped PbO_2. Some applications in the field of ozone generation and pollutant incineration are described.

EXPERIMENTAL

All experimentals were conducted using Fluka or Aldrich chemicals. The electrochemical experiments were carried out using an EG&G/PARC model 273A potentiostat with EG&G software. For the impedance measurements, an EG&G model 5210 lock-in amplifier was used. All potentials are referred to Ag|AgCl|KCl (sat.) unless otherwise stated.

Lead dioxide deposits were grown from a 0.1 M $Pb(NO_3)_2$ + 0.1M HNO_3 solution. For doping with cations, the corresponding nitrate salt (0.01 M) was added to the solution. Fluoride was added as the sodium salt.

X-Ray photoelectron spectroscopy (XPS) measurements were carried our using a Perkin-Elmer φ 5600ci instrument. In the radiotracer experiments, the electrodes were weighed after deposition and then dissolved in 5 ml H_2O containing 0.1 ml acetic acid and 0.05 ml H_2O_2. Then the activity was measured by the scintillation method.

RESULTS AND DISCUSSION

Electrodeposition

The conditions employed for the electrodeposition have a great influence on the properties and reactivity of the resulting films, although, especially in the case of doped electrodes, there seems to be no universal strategy which can be adopted and every system needs to be separately analysed.

It has been found that variations of the conditions of PbO_2 electroplating cause changes in the oxide properties, which result in different electrocatalytic behaviour. In this section, the electrodeposition of PbO_2 films from nitrate solutions and the physicochemical properties of the resulting oxide are discussed.

Experiments on the electrodeposition of PbO_2 on Pt RDE showed that the reaction orders for Pb(II) and H^+ ions are one and zero, respectively. The number of electrons involved in the rate determining step, calculated from the voltammetric data, was one. The effective activation energy of the reaction were 70 kJ/mol and 12 kJ/mol at low and high overpotentials, respectively, These data indicate that at low overpotentials the PbO_2 electrodeposition is limited by an electron transfer stage. Increasing the electrode potential led to a change of the limiting step from a kinetic to a diffusion controlled one. According to these data, in nitrate solutions the first stage of the reaction is the formation of oxygen con-

taining species, such as chemisorbed OH-radicals, followed by a chemical step in which these particles interact with the lead species forming a soluble intermediate product, likely to contain Pb(III), which is then oxidised electrochemically forming PbO_2.[3]

The influence of the electrodeposition conditions (electrodeposition potential, pH and temperature of the solution) on the phase composition was studied by XRD.[4] The films consisted of a mixture of α- and β-phases of PbO_2 in most cases. In the potential range 1.3 – 1.5 V, the electrodeposition potential and pH value (in the range 1 – 3) had hardly any influence on the amount of the α-phase. On the other hand, a decrease of the relative intensity of the α-phase peaks with increasing pH (in the range 1 – 3) was observed for films grown at potentials higher than 1.5 V. In particular, the decrease was sharp for electrodeposition potentials positive of 1.5 V and as the solution temperature increased. When the temperature of the deposition electrolyte was 65 ºC, only the β-phase of PbO_2 was detected. It is interesting to note that a strong change of the crystalline orientations for the β-phase was observed as a function of the electrodeposition conditions. For instance, the ratio of the relative intensity of the (110) to (101) plane decreased with increasing electrodeposition potential and decreasing solution temperature.

Proton inclusion and PbO_2 doping

In addition to affecting the crystallographic characteristics of the electrodeposited PbO_2, the above cited experimental parameters affect the stoichiometry of the two PbO_2 allotropic forms (α and β). It is known that both of these deviate from stoichiometry, and that these deviations are more pronounced for electrochemically prepared oxide than for chemically obtained samples, and for the α-PbO_2 more than for the β-PbO_2 form.

It is now widely believed that the reason of this non-stoichiometry is the presence of lead vacancies in the crystallographic structure. In the model recently proposed by Ruetschi,[5] these vacancies are arranged to form layers (named "internal surfaces") between crystallographically ordered areas, and the charge of each missing Pb^{4+} ion is compensated by only OH^- ions or by both Pb^{2+} and OH^- ions. Thus, the following formula has been proposed for a better description of the composition of PbO_2.[5]

$$Pb_{(1-x-y)}^{4+} Pb_y^{2+} OH_{(2-4x-2y)}^{2-} OH_{(4x+2y)}^{-} \qquad (1)$$
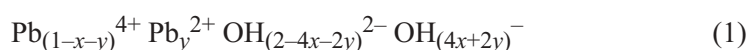
The model accounts for the fact that experimental studies report evidence for the presence of Pb(II)[5] and structural water[6–12] in the PbO_2 lattice. These studies generally recognise that there is a proportionality between the hydrogen content of a PbO_2 electrode and its electrochemical activity.[13] It seems, however, that there has not been sufficient systematic investigation on how the control of different parameters in the electrodeposition of PbO_2 can affect the amount of structural water in the resulting oxide. The effect of subsequent treatment following electrodeposition, such as heating, would also merit some further study. It is known, for example, that heat treated electrodes are more active in the production of ozone at high potentials.[14]

In the framework of this, we used the radiotracer method to investigate the experimental parameters, including doping, that affect the inclusion of tritium into PbO_2 layers electrodeposited galvanostatically onto platinized titanium substrates. Both α-PbO_2
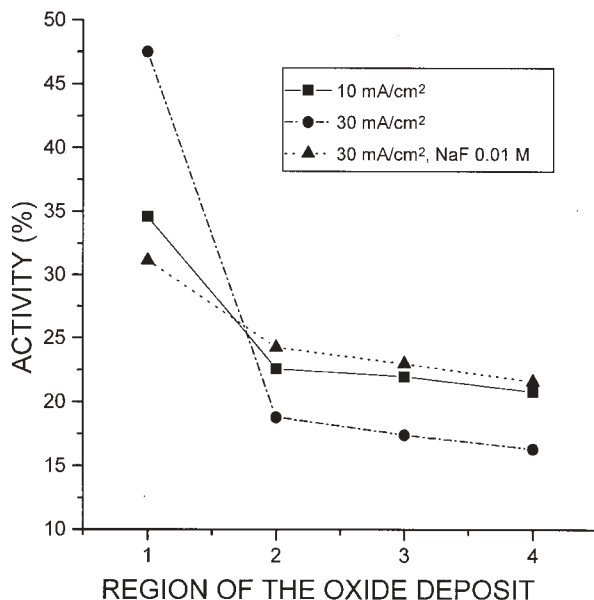
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Fig. 1. Percent radiochemical activity of tritium incorporated into an electrodeposited PbO_2 as a function of step-by-step etching of the sample in a CH_3COOH/H_2O_2 solution. Region 1: 1 μm etched; Region 2: further etching of 2 μm; Region 3: further etching of 2 μm; Region 4: further etching of 3 μm. See also text for more details. The effect of the electrodeposition current and of the presence of F^- is shown.

and β-PbO_2 were examined, although the latter received more attention.

The distributions of tritium incorporated into various layers of β-PbO_2 electrodeposited from T_2O and having a thickness of 10 μm are shown in Fig. 1. The data reported are the results of a stepwise etching of the oxide deposit in a CH_3COOH/H_2O_2 solution. The samples were immersed in the etching solution for fixed periods of time; each time the weight loss was then determined gravimetrically after washing with dry acetone and the radiochemical activity of the solution was measured. The amount of tritium incorporated into different regions of the oxide layer can then be calculated (Fig. 1) as the percent of the activity of the whole deposit taken as 100 %. The reported data are the average of 5 stepwise experiments.

It is interesting to note that with the higher electrodeposition current density, a large fraction of tritium (protons) is concentrated in the surface region, indicating that a relatively rapid growth of a deposit tends to segregate defective sites in this region. In contrast, the F-doped PbO_2 features a reasonable decrease in tritium in the surface layer. This is due to the fact that F^- can replace adsorbed H_2O and/or the isoelectronic OH groups.[1]

As part of an effort to gain insight into doped PbO_2 with improved electrochemical characteristics, we have recently started a detailed investigation of Fe-doped PbO_2.[2] The electrodeposition of the doped lead dioxide was studied on a Pt electrode in HNO_3 containing $Pb(NO_3)_2$ and $Fe(NO_3)_3$. Again, the radiotracer technique, using [55]Fe, proved to be potent means for investigating the factors that influence the incorporation of iron.

The presence of Fe(III)-ions in the electrodeposition solution causes only a slight increase in the lead dioxide electrodeposition rate without seemingly changing the deposition mechanism.[15] However, despite the low content of iron in the bulk lead dioxide, Fe(III) reasonably affects the catalytic and mechanical properties of the iron-doped

PbO_2. For the utilization of the resulting oxide properties, it is quite important to know the influence of the preparation conditions of the Fe-doped PbO_2 on the content of iron in the bulk oxide. Thus, increasing the iron concentration in the electrodeposition solution leads to an increase in the Fe content in the bulk oxide (Table I).

TABLE I. The influence of the electrolyte on the Fe content in the deposited PbO_2. $E_{dep} = 1.6$ V (Ag|AgCl)

Deposition electrolyte	Fe content / weight %
0.1 M HNO_3 + 0.1 M $Pb(NO_3)_2$ +	
+ 0.1 M $Fe(NO_3)_3$	0.0108
+ 0.05 M $Fe(NO_3)_3$	0.0247
+ 0.07 M $Fe(NO_3)_3$	0.0427

Taking into account the low content of Fe, it can be suggested that its incorporation into the lead dioxide is due to its physical adsorption on the electrode surface. Good support for this conclusion is given by the effect of the electrodeposition potential (Table II) (or the current density) on the iron content. According to the value of the zero charge potential of a PbO_2 electrode (0.91 ± 0.1 V *vs.* SCE[16]), under the present electrodeposition conditions, the electrode surface is always positively charged, which is the most likely reason for the low content of Fe in the bulk oxide. With increasing potential or current density, the iron content is strongly decreased (Table II) due to the increase of the positive charge of the electrode.

TABLE II. Influence of the deposition voltage on the Fe content in electrodeposited PbO_2. Deposition solition: 0.1 M $NaNO_3$ + 0.1 M $Pb(NO_3)_2$ + 0.01 M $Fe(NO_3)_3$ (pH 2.3)

Deposition potential / V (*vs.* Ag|AgCl)	Fe content / weight %
1.50	0.0402
1.60	0.0205
1.70	0.0157

According to our suggestion, another way to increase the iron content in lead dioxide is to decrease positive charge of the Fe-ions, for instance by favouring hydrolysis which leads to the formation of different OH-containing compounds with a lower positive charge like $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and $Fe(OH)_3$. We did indeed observe an increase of the Fe content with increasing pH of the electrodeposition solution (Table III). The same effect was observed on increasing the temperature of the electrodeposition solution. In this case, the rate of hydrolysis was increased and the solution became yellow due to the formation of OH-containing Fe complexes. It is also interesting to note that an enhanced incorporation of Fe was observed if fluoride-ions were also present in the electrodeposition solution. This effect may be connected with the formation of a complex of fluoride with iron with a relatively high negative charge, such as $[FeF_6]^{3-}$.

TABLE III. Influence of the HNO_3 concentration on the Fe content in electrodeposited PbO_2. $E_{dep} =$ 1.6 V (Ag|AgCl)

Deposition electrolyte	Fe content / weight %
0.1 M Pb(NO)$_3$ + 0.01 M Fe(NO$_3$)$_3$ +	
+ 0.10 M HNO$_3$	0.0108
+ 0.25 M HNO$_3$	0.0067
+ 0.50 M HNO$_3$	0.0028

In a series of experiments SIMS and XPS were employed to characterise doped PbO_2 layers electrodeposited on Pt-Ti under conditions in which the β- form of the oxide largely prevails. In previous work on the XPS of PbO_2,[9] the importance of the examination of the O_{1s} region was pointed out as it provides information on the hydration state of the surface. The XPS spectrum in the O_{1s} region for PbO_2 shows two peaks; a broad one at higher binding energy which corresponds to adsorbed H_2O and/or OH, and a lower binding energy one which corresponds to lattice oxygen.
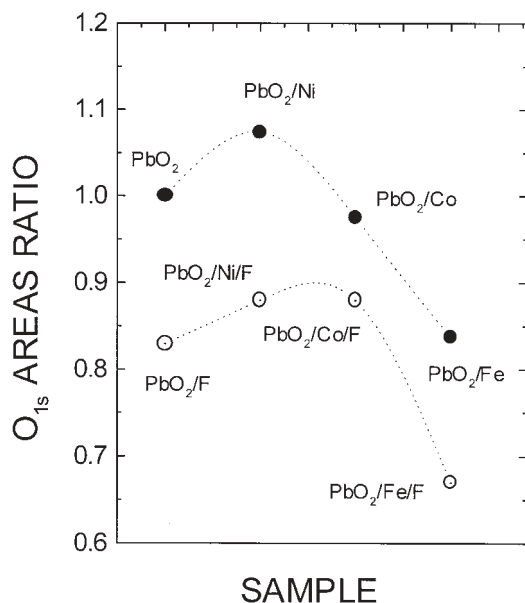

Fig. 2. Ratios of the areas of the O_{1s} XPS signal for different doped PbO_2 samples to that of non-doped PbO_2.

In this work, the effects of doping with F^-, with cations (Fe^{3+}, Co^{2+} and Ni^{2+}) and with cations together with F^- were examined. These dopants have been found to cause different, reasonable variations only for the higher binding energy peak, indicating changes in the interaction of water with the surface.

The areas of the O_{1s} signals for the doped systems, normalised to that of non-doped PbO_2, are displayed in Fig. 2. It is seen that Ni–PbO_2 and Fe–PbO_2 have opposing effects on the amount of surface adsorbed water and OH groups; in the first case there is an accumulation and in the second one a marked decrease compared with non-doped PbO_2. This trend is still observed when F^- is used as a co-dopant.
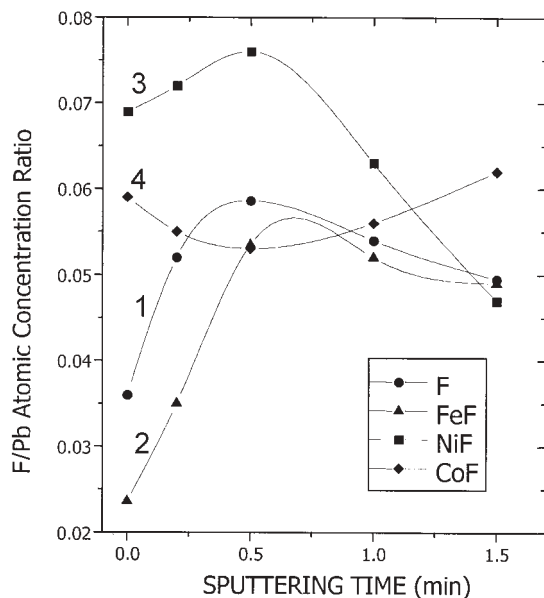
Fig. 3. XPS experiments showing the F/Pb_{4f} atomic concentration (%) ratios as a function of sputtering for PbO_2 doped with F^- or simultaneously with fluorine and metal cations.

From Fig. 3 it can be seen that the F/Pb atomic ratio for most of the examined systems increases after 0.5 min sputtering and then decreases to a common value as sputtering is continued. The exception to this trend is the $(Co^{2+}–F^-)$ doped PbO_2 for which the ratio is essentially constant.

Interestingly, Ni is seen to favour both an accumulation (Fig. 2) as well as the incorporation of F^-. On the basis of the data of Figs. 2 and 3, the observed decrease of surface oxygen for co-doped $(Ni–F)–PbO_2$ (Fig. 2) is attributable to the effect of F^-. Conversely, for the $(Fe–F)–PbO_2$ system, the amount of F^- at the surface is relatively low, and this suggests that both dopants contribute to the observed decrease of the surface H_2O/OH (Fig. 2). Moreover, we are of the opinion that the observed behaviour as a function of sputtering time can probably be explained by the presence of an iron-fluoride complex at the surface.

The SIMS data show evidence of PbO_xF_y clusters in samples prepared from fluoride. Moreover, the depth profiles show a maximum in fluorine near the surface, indicating that this is a region of F^- enrichment, in agreement with the XPS data.

Doped PbO_2 electrodes and ozone electrogeneration

Ozonization has long been used for the treatment of drinking water where, compared with the commonly employed chlorination method, it has the important advantage that its decomposition products are environmentally acceptable. Within this field of research, we recently proposed the *"cathodic oxidation method"* of treating pollutants[17,18] in which a O_2 stream is used to sweep the O_2/O_3 gas mixture produced at a PbO_2 anode into the cathodic compartment of the same electrochemical cell containing the polluting species. The hydrogen peroxide formed at the cathode reacts with O_3 giving rise to a highly oxidising environment. We compared the results obtained with those of direct electrolysis at the PbO_2 anodes.
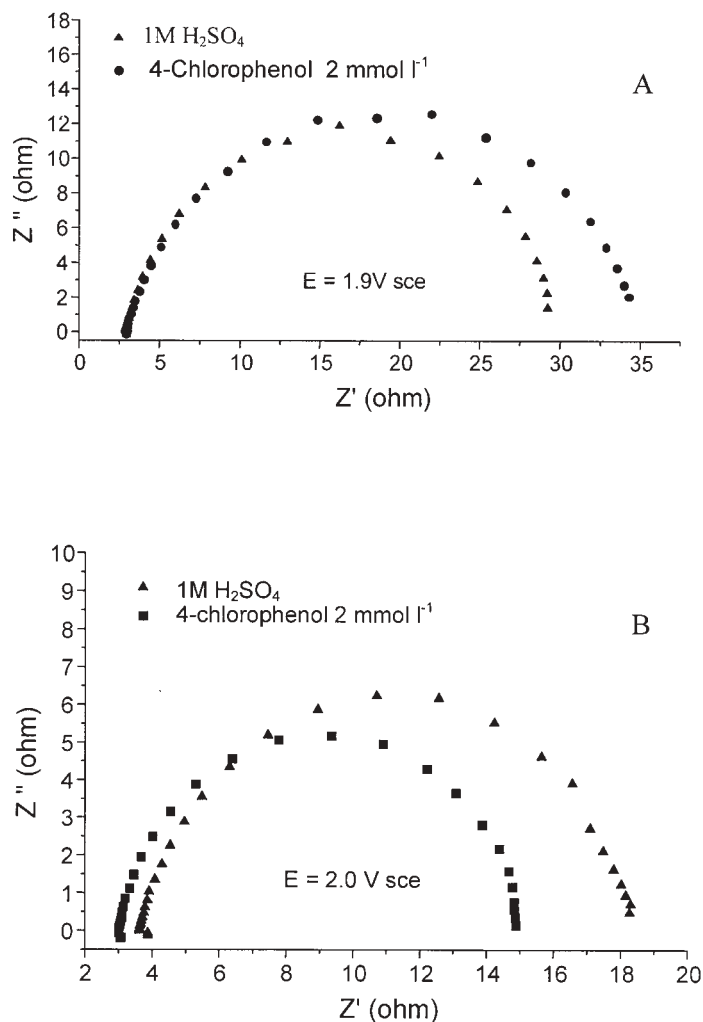
Fig. 4. Impedance plots for PbO_2 in 1 M H_2SO_4 in the presence and in the absence of $2×10^{-3}$ M 4-chlorophenol.

In itself, the direct electrolysis of, for example, 4-chlorophenol reveals very interesting aspects from the mechanistic point of view. Thus, the impedance data of Fig. 4 show that even up to potentials as high as 1.9 V *vs.* SCE, the electro-oxidation of organic compound is not prevalent over the discharge of water (Fig. 4A), despite the fact that *h*-chlorophenol oxidation does indeed occur. As can be seen from Fig. 4B, preferential oxidation occurs at higher potentials. Thus, over a relatively wide potential range, the oxidation of the organic compound is a process that is mediated by OH radicals derived from the oxidation of water.

From the point of view of an efficient incineration of organic pollutants, our comparative studies show that the "*cathodic oxidation*" approach gives considerably better results, and it emerges as a very promising one for application in detoxification processes.[17,18]
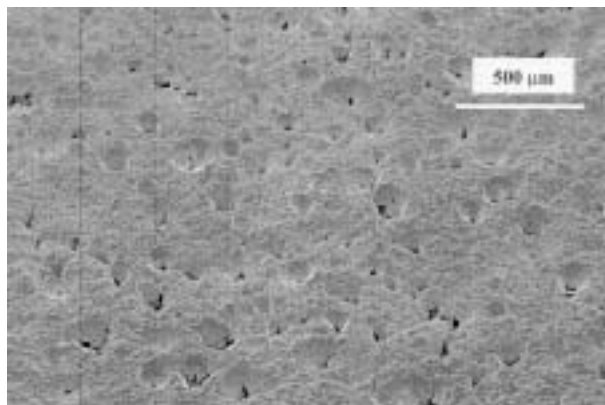
Fig. 5. SEM micrograph of PbO_2 electrodeposited on a platinised porous titanium support.

The encouraging results obtained using O_3 mediated incineration of pollutants provided further stimulus to our research on the improvement of the efficiency of electrochemical ozone formation. We have shown[19] that electrodeposition of PbO_2 in the presence of Fe(III) or Co(II)produces doped material which are stable and have a high electrocatalytic activity for ozone generation. This activity can be further enhanced if the Fe-doped and Co-doped oxides are deposited on platinised porous titanium substrates. A representative SEM micrograph is given in Fig. 5.

Experiments were carried out in 1 M H_2SO_4 and in phosphate buffer, at room temperature and at 3 ± 1 ºC. In 1 M H_2SO_4, the current yield of O_3 formation reached 20 % with Fe–PbO_2 and 12 % with Co–PbO_2 at 3 ± 1 ºC. In the phosphate buffer electrolyte, the current yields were 14 – 16 % with Fe – PbO_2 and 15–18 % with Co–PbO_2 at 4 ± 1 ºC. One important aspect that should be stressed is that these data were obtained at constant current densities between 50–70 mA/cm^2, which are relatively low values for these kind of studies. Particularly in the case of Co–PbO_2, doping improves the electrode stability against corrosion.

CONCLUDING REMARKS

In this paper some of our recent work on the study of factors that influence the electrochemical behaviour of electrodeposited PbO_2 are briefly reviewed. In particular, doping of PbO_2 with cations (Fe^{3+}, Co^{2+} and Ni^{2+}), with F^- and with cations and F^- simultaneously is discussed as a way of improving the stability and electrochemical activity in processes occurring at high potentials such as perchlorate, peroxysulphate and ozone, and in studies on the breakdown of pollutants by electrochemical methods.

The experimental conditions chosen for the electrodeposition strongly influence the proton content (*i.e.,* the defective structure) of the oxide. Radiotracer experiments show that high electrodeposition current densities favour the segregation of incorporated tritium (protons) in the surface. On the other hand, fluorine doping results in a marked decrease in the surface oxygen species. The effect of doping with metal cations strongly depends on the nature of the metal. Thus, the effect of iron is similar to that of fluorine, while with nickel one observes an accumulation of surface oxygen species.

Fe and Co doped PbO_2 on porous titanium substrates have a high efficiency for the electrogeneration of ozone. We consider this result to be particularly important considering our recently proposed *"cathodic oxidation method"*, *i.e.,* an ozone mediated electrochemical method for the destruction of pollutants in the cathodic compartment of an electrochemical cell.

И З В О Д

ОЛОВО-ДИОКСИДНЕ ЕЛЕКТРОДЕ ЗА АНОДНЕ ПРОЦЕСЕ НА ВИСОКИМ ПОТЕНЦИЈАЛИМА

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Разматрано је доповање PbO_2 катјонима (Fe^{3+}, Co^{2+}, Ni^{2+}), флуоридним јоном и симултано катјонима и F^- јоном, као пут за побољшање активности и електрохемијске активности за процесе који се одигравају на високим потенцијалима. Један од ефеката доповања је контрола количине структриране воде у оксиду. Експерименти радиообележивачима показују да високе густине струје електродепозиције фаворизују сегрегацију инкорпорираног трицијума (протона) на површини. На другој страни доповање флуором знатно смањује присуство кисеоничних врста на површини. Утицај доповања металним катјонима јако зависи од природе метала. Гвожђе се понаша као флуор, док никал проузрокује акумулацију кисеоничних честица на површини. Доповане PbO_2 електроде показују сасвим добру активност за електрогенерисање озона. Fe и Co доповани PbO_2 показао је искоришћење струје овог процеса 15–20 %. Овај резултат је значајан за наше ново проучавање "катодне оксидације", тј. посредног електрохемијског метода у којем се струја O_2 користи да пренесе гасну смешу O_2/O_3 sa PbO_2 аноде у катодни простор исте електрохемијске ћелије са полутантима.

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