

Oxidation of toluene on Bi-doped PbO₂ studied by electrochemical impedance spectroscopy and UV spectrophotometry

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Abstract Oxidation of organics in the potential region of O₂ evolution is supposed to proceed through the oxidation of water to hydroxyl radicals, which then may either be further oxidized to give molecular oxygen or interact with organic molecules in an oxygen transfer reaction. Therefore, the electrode material must ensure (1) the preferential adsorption of the organic compound, (2) the production of adsorbed hydroxyl radicals able to react with this compound in a selective oxidation reaction (with as little as possible oxygen evolution), and (3) a long-term stability. In the present paper, the oxidative decomposition of toluene in sulfuric acid solution on PbO₂ coatings deposited on Ti substrate from acidic nitrate+fluoride baths containing Pb²⁺ and Bi³⁺ is investigated by voltammetry, electrochemical impedance spectroscopy, and UV spectrophotometry. The chemical composition and structure of the catalytic coatings is characterized with X-ray photoelectron spectroscopy and X-ray diffraction. The catalytic activity is estimated both from current density vs potential and polarization resistance vs potential plots using measurements on the same electrodes in sulfuric acid without toluene to eliminate the oxygen evolution reaction that proceeds in parallel to the oxidation of toluene. A skeletal reaction mechanism of the process is proposed to account for the steady-state and transient response of the catalytic electrodes during oxidation of toluene.

Keywords Lead dioxide · Bismuth doping · Toluene · Electro-oxidation · Reaction mechanism

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Introduction

One of the important utilities in an individual water purification kit is a catalytic device able to perform effective decontamination and purification of waters from prospective but unknown water sources for personal use. Such a device must be built upon an effective, miniature, and long-lasting catalytic material. The overall goal of the present project is to develop technologies for the electro-deposition of mixed oxide coatings with catalytic activity towards the oxidative degradation of organic compounds and with regard to their use in such a catalytic device.

Oxidation of organics in the potential region of O₂ evolution is supposed to proceed through the oxidation of water to hydroxyl radicals, which then may either be further oxidized to give molecular oxygen or interact with organic molecules in an oxygen transfer reaction. Therefore, the catalytic electrode material must ensure (1) the preferential adsorption of the organic compound in question, (2) the production of adsorbed hydroxyl radicals able to react with organics in a selective oxidation reaction (with as little oxygen evolution as possible), and (3) a reasonably long service life. Among a wide range of catalytic materials, mixed and composite oxides have been widely investigated in view of their stability under oxidative conditions [1–14]. PbO₂ is one of the most studied anode materials owing to its large electronic conductivity, chemical stability, and low cost [1–14]. This type of anode material is still widely used for electrochemical treatment of wastewater [14] despite the promising alternative of anodically treated conductive diamond electrodes that have been extensively investigated in recent years [15–18]. Two basic pathways are envisaged for the optimization of lead dioxide properties: homogeneous doping [1–7] and composite formation [8–12]. In the present paper, the catalytic activity of PbO₂ coatings

deposited on Ti from acidic nitrate baths containing Pb^{2+} and Bi^{3+} towards oxidative decomposition of toluene in sulfuric acid solution is investigated by voltammetric and electrochemical impedance spectroscopic measurements. The kinetics of decomposition of toluene has been followed by UV spectrophotometry. As a result of this investigation, a skeletal mechanism of the process is proposed and quantitatively compared to the electrochemical data. It is regarded as a first approach to a deterministic tool for the optimization of the electro-catalytic properties and the extent of service life of the catalytic coatings in future work.

Experimental

The substrate material was pure Ti (99.9%), and disc electrodes covered with acid-resistant lacquer and embedded in epoxy resin were used (exposed area 0.8 cm^2). Their pretreatment consisted of mechanical abrasion with emery paper up to 1200 grade, followed by etching in 5% hydrofluoric acid (HF) for 10 s. A conventional three-electrode cell featuring a Pt mesh counter electrode and a saturated calomel reference electrode was employed. The electrolytes for the anodic electrodeposition of the catalysts were $1 \text{ M HNO}_3 + 0.5 \text{ M Pb}(\text{NO}_3)_2 + 0.1\% \text{ HF}$ with and without the addition of 0.05 M or $0.1 \text{ M Bi}(\text{NO}_3)_3$. The electrodeposition of the Bi-doped PbO_2 was carried out as a two-step procedure, in certain analogy to that reported in [19]. First, undoped PbO_2 was deposited at 1.65 V vs SCE for typically 2 h; then, the solution was changed to that containing the dopant Bi^{3+} ion, and further deposition for 2 h at 1.7 V vs SCE was carried out. Through preliminary measurements, it was found that this two-step procedure results in a dense coating that had the best adhesion to the substrate.

Oxidation of toluene was carried out in $0.5 \text{ M H}_2\text{SO}_4$ containing 0.005 M of $\text{C}_6\text{H}_5\text{CH}_3$ (the solubility of toluene in water at ambient temperature has been quoted to be of the order of 0.006 M). All solutions were prepared from p.a. chemicals and bi-distilled water. The electrochemical measurements were performed with an Autolab PGSTAT 30 with a FRA2 module driven by GPES 4.9 and FRA 4.9 software (EcoChemie, The Netherlands). Potentiostatic current vs potential curves and impedance spectra at different potentials were registered (AC amplitude 10 mV , frequency range $10 \text{ mHz} - 100 \text{ kHz}$). The fitting of the impedance spectra with a suitable transfer function was carried out via user subroutines of an Origin 7.5 software platform. X-ray photoemission spectroscopy (XPS) studies were carried out using an ESCALAB Mk II (VG Scientific) electron spectrometer with a base pressure of $\sim 10^{-7} \text{ Pa}$. The photoelectrons were excited with $\text{Mg K}\alpha$ ($1,253.6 \text{ eV}$) X-ray source, and the analyzer pass energy was 20 eV . The

$\text{C}1s$, $\text{O}1s$, $\text{Pb}4f$, $\text{Bi}4f$, and $\text{Ti}2p$ photoelectron lines were recorded, and the binding energies were calibrated vs the $\text{C}1s$ peak. X-ray diffractograms were obtained on a Philips APD15 apparatus using a $\text{Cu K}\alpha$ source.

Results and discussion

Figure 1 shows the steady-state current vs potential curves for the oxidation of toluene on pure and doped PbO_2 in $0.5 \text{ M H}_2\text{SO}_4 + 0.005 \text{ M C}_6\text{H}_5\text{CH}_3$. They were obtained by subtracting the current obtained on the same materials in pure $0.5 \text{ M H}_2\text{SO}_4$. The values of the currents demonstrate that the catalytic activity of Bi- PbO_2 towards the electro-oxidation of toluene is significant, in accordance to reports by earlier authors using voltammetric measurements [1]. At potentials close to the open circuit potential (about 1.3 V), the catalytic activity is only slightly dependent on the concentration of Bi in the solution used for the anodic electrodeposition of the oxides, whereas in the potential range $1.45 - 1.60 \text{ V}$ the catalytic activity of the coating obtained from a bath that contained 0.1 M Bi^{3+} is significantly higher.

Impedance spectra registered in the range of potentials in which oxidation of toluene proceeds on Bi-doped PbO_2 (prepared from a solution containing 0.1 M Bi^{3+}) are presented in Fig. 2, whereas the corresponding spectra of the same electrode in a blank $0.5 \text{ M H}_2\text{SO}_4$ are collected in Fig. 3. On comparing the two figures, the extent of oxidation of toluene is evidenced both by the significantly smaller values of the impedance at very low frequencies and the presence of additional time constants at medium and low frequencies probably related with adsorption of intermediate species and a subsequent homogeneous

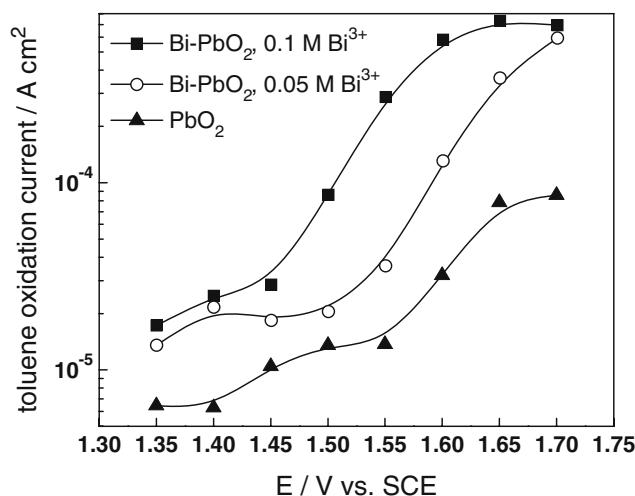
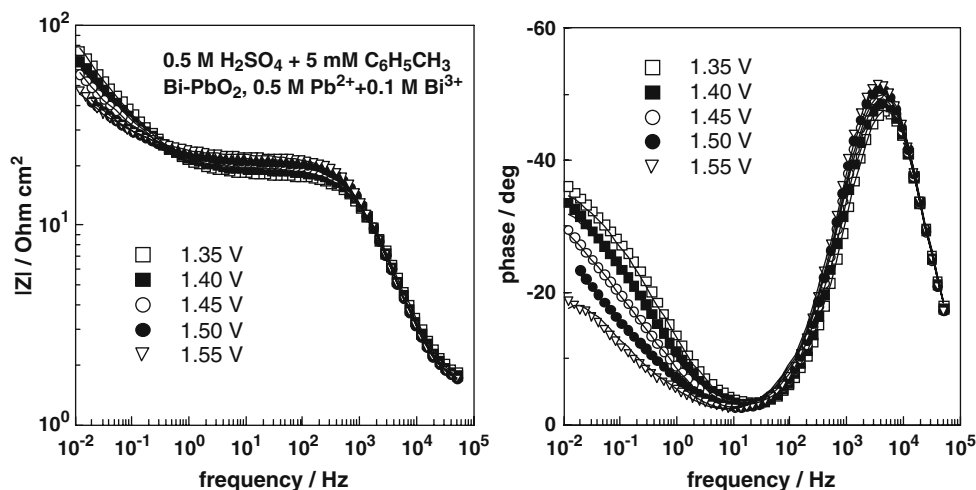


Fig. 1 Current vs potential curves for the oxidation of 0.005 M toluene on pure and Bi-doped PbO_2 in $0.5 \text{ M H}_2\text{SO}_4$

Fig. 2 Impedance spectra during oxidation of 0.005 M toluene in 0.5 M H₂SO₄ on a Bi-doped PbO₂ prepared from a solution containing 0.1 M Bi³⁺. Points, experimental values; solid lines, best-fit calculation according to the transfer function described in the text



chemical reaction. The effect of changing the deposition conditions of the catalyst on the impedance spectra is illustrated in Fig. 4, in which the results on the oxidative decomposition of toluene on Bi–PbO₂ formed in the presence of 0.05 M Bi³⁺ are summarized. It can be stated that the effect of lowering the concentration of Bi in the electrodeposition bath on the toluene decomposition rate is relatively small, the difference between the spectra being evident in the low-frequency range only (cf. Figs. 3 and 4). On the other hand, it has been found that the rate of decomposition of toluene on pure PbO₂ is on the overall negligible, as shown also by earlier authors [1].

The phase angle vs frequency curves depicted in Figs. 2 and 4 suggest the presence of three time constants in the system. The high-frequency time constant at 1–10 kHz is probably related to both the electric properties of the TiO₂ layer formed on the Ti substrate and the charge transfer process of oxidation of toluene. The medium frequency time constant observed as a shoulder in the curves at 1–10 Hz can be ascribed to the relaxation of the coverage

of an adsorbed intermediate, whereas the low frequency part of the spectra is best described by the impedance of a subsequent homogeneous chemical reaction in the electrolyte. Based on these considerations, the following transfer function has been found to be appropriate for the treatment of the impedance data in the presence of toluene:

$$Z = R_{el} + \frac{1}{\frac{1}{Z_Y} + \frac{1}{R_t + \frac{1}{j\omega C_a + \frac{1}{R_a + Z_G}}} \tag{1}$$

where R_{el} is the resistance of the electrolyte, R_t is the charge transfer resistance, R_a is the resistance of the adsorption process, and C_a the adsorption pseudo-capacitance. In this function, Z_Y is the Young impedance describing the electric properties of the TiO₂ layer [20]:

$$Z_Y = \frac{p}{j\omega C} \ln \left(\frac{1 + j\omega \rho_d \epsilon \epsilon_0 e^{\frac{1}{p}}}{1 + j\omega \rho_d \epsilon \epsilon_0} \right) \tag{2}$$

Fig. 3 Impedance spectra of a Bi-doped PbO₂ prepared from a solution containing 0.1 M Bi³⁺ in 0.5 M H₂SO₄ without toluene

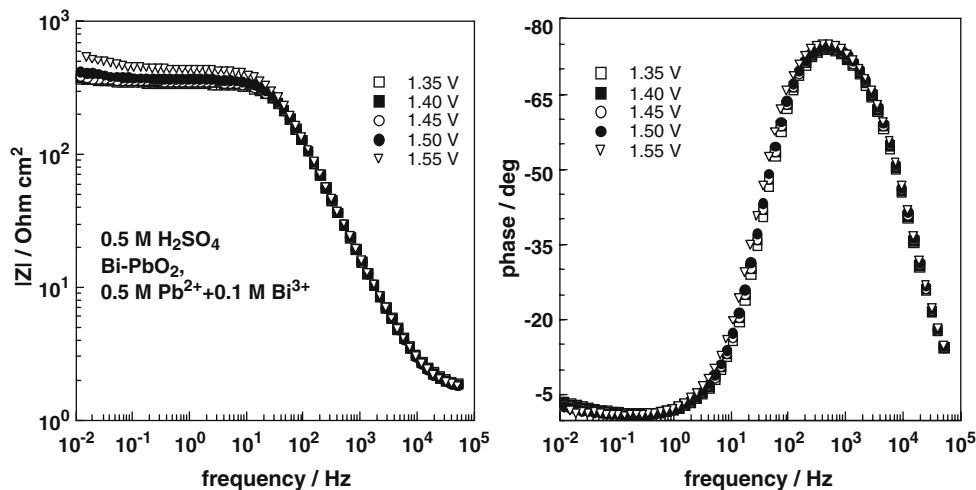
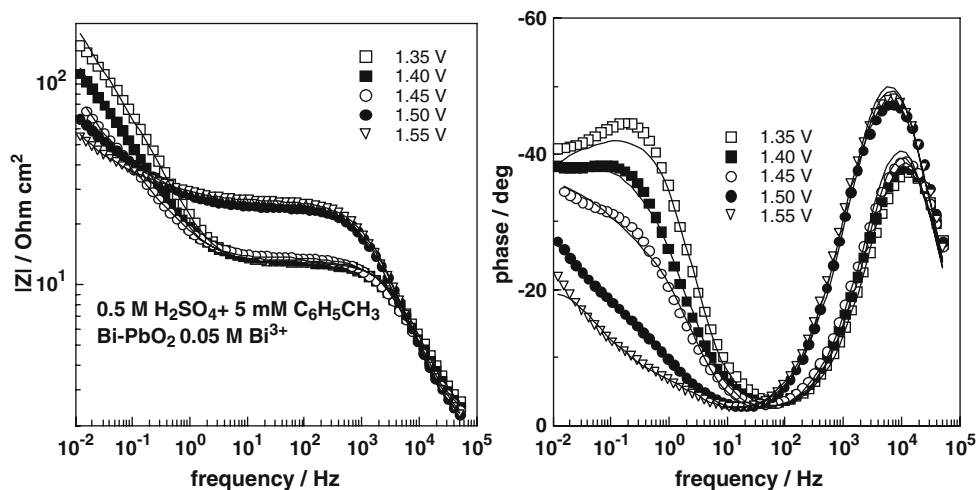


Fig. 4 Impedance spectra during oxidation of 0.005 M toluene in 0.5 M H₂SO₄ on a Bi-doped PbO₂ prepared from a solution containing 0.05 M Bi³⁺. Points, experimental values; solid lines, best-fit calculation according to the transfer function described in the text



In the formal sense, the Young impedance presumes an exponential decay of the defect-induced conductivity of an insulating layer from the interface at which the defects are injected; thus, it is suitable for the description of the dielectric properties of the anodic oxide on Ti. In the Young impedance function (Eq. 2), *C* is the layer capacitance, *p* is the relative permeation depth of defects in this layer, ρ_d is the resistivity at the interface at which such defects are generated, and ϵ is the dielectric permittivity of the layer.

Furthermore, in the transfer function described by Eq. 1, *Z_G* stands for the so-called Gerischer impedance [21]

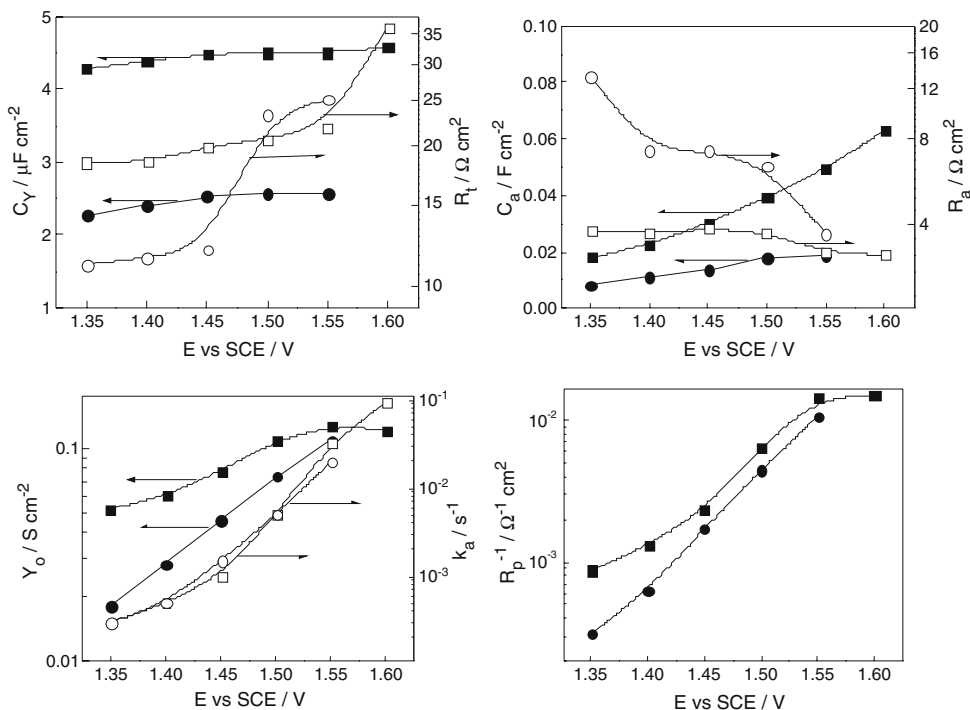
describing the frequency response of a subsequent homogeneous chemical reaction:

$$Z_G = Z_O \left(\sqrt{\frac{\omega^2 + k^2}{\omega^2 + k^2} + k} - j \sqrt{\frac{\omega^2 + k^2}{\omega^2 + k^2} - k} \right) \quad (3)$$

where $Z_O = \frac{RT}{(nF)^2 c \sqrt{Dk}}$, \bar{c} is the steady-state concentration of the soluble intermediate, *D* is its diffusion coefficient, and *k* is a formal rate constant.

Fits to the transfer function described by Eqs. 1–3 are presented in Figs. 2 and 4 and demonstrate that the pro-

Fig. 5 Parameters of the transfer function determined by best-fit calculation of the experimental impedance data as a function of potential. Circles, deposition from a bath containing 0.05 M Bi³⁺; squares, 0.1 M Bi³⁺



posed function can satisfactorily account for the experimental data in the whole investigated range of potentials. The main parameters extracted from the fitting procedure for Bi–PbO₂ electrodes produced from solutions containing 0.05 or 0.1 M Bi³⁺ are collected in Fig. 5. The following conclusions can be drawn from the values of the parameter estimates as depending on potential:

- The capacitance of the TiO₂ layer is approximately constant, indicating that no further growth of this layer proceeds in the investigated potential window and the current is consumed for anodic charge transfer reactions.
- The apparent charge transfer resistance is constant at low potentials (below 1.55 V in the case of an electrode deposited from a solution containing 0.1 M Bi³⁺ and below 1.5 V for that deposited from a 0.05 M Bi³⁺ containing electrolyte) indicating that the charge transfer reaction is probably controlled by migration of electronic defects through the TiO₂ layer.
- The adsorption resistance, in general, decreases with increasing potential, its values being larger for the electrode deposited from a solution containing less Bi³⁺, and vice versa for the adsorption pseudo-capacitance. This may mean that the adsorption/desorption step is controlled both by potential and the availability of Bi sites at the electrode surface.
- Both parameters of the Gerischer impedance increase quasi-exponentially with potential indicating that charge transfer is probably involved in the homogeneous reaction as well.

The values of the inverse of the polarization resistance $R_p = [R_t + R_a + 1/(Y_o k^{1/2})]$ are also collected in Fig. 5 for the two Bi–PbO₂ electrode types. Their dependence on potential is largely analogous to that of the steady-state current densities (Fig. 1), which indicate that they can be used also as estimate of the overall catalytic activity of the electrodes towards oxidative decomposition of toluene. The value of the product $2.3R_p i$ has been estimated at around 0.045 V indicating a two-electron transfer during the rate-limiting step of the overall reaction.

To estimate quantitatively the extent of electrochemical oxidation of toluene, UV–vis spectra of the solution have been registered during polarization at 1.35 and 1.40 V for 2 h (Fig. 6). During the oxidation, the toluene oxidation current density values were analogous to those shown in Fig. 1 for the respective potentials, the quantities of charge passed have been estimated as 0.12 C cm⁻² (at 1.35 V) and 0.18 C cm⁻² (at 1.40 V). The obtained spectra demonstrate that an efficient oxidation of 0.005 M toluene to CO₂ is achieved, as demonstrated by the drop in intensity of all the peaks in the spectra. For times of oxidation ≥ 120 min, some intermediate products appear to be generated. The spectra were fitted using a combination of four Gaussian-type peaks, the correspondence between the calculated curves and experimental data being satisfactory as evidenced in Fig. 6. The dependencies of the peak intensities and peak positions on oxidation time are shown in Fig. 7. The intensities of the peaks 3 and 4 decrease quasi-exponentially with the time of oxidation indicating a pseudo first order of

Fig. 6 UV–vis spectra at different times of oxidation of 0.005 M toluene in 0.5 M H₂SO₄ on Bi–PbO₂ at a potential of 1.35 V

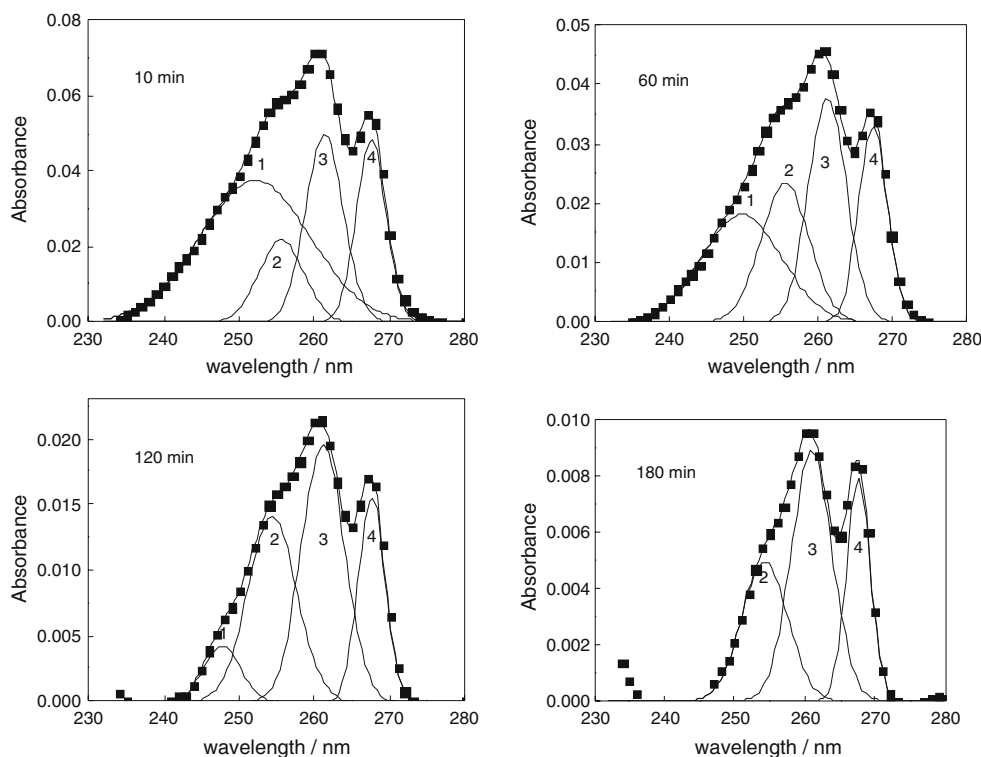
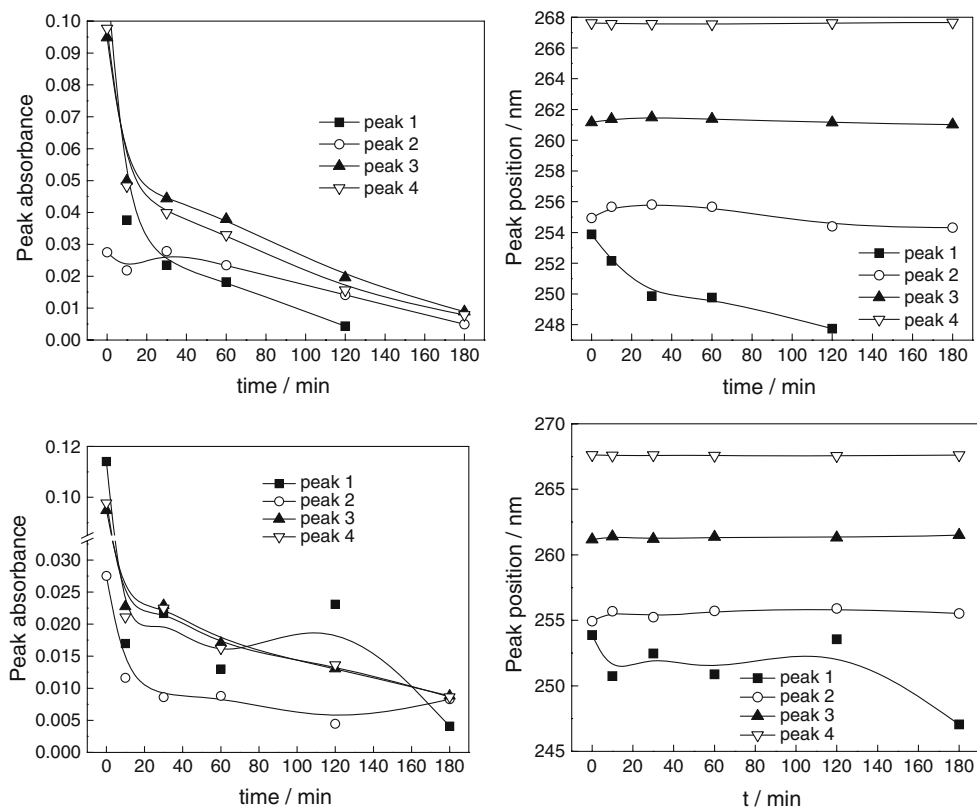


Fig. 7 Dependences of the peak intensities (*left*) and peak positions (*right*) on the oxidation time of 0.005 M toluene in 0.5 M H₂SO₄ on Bi–PbO₂ at 1.35 V (*above*) and 1.40 V (*below*)



the rate-determining step of toluene oxidation. On the other hand, there is a non-monotonous change in both the peak intensity and position of peak nos. 1 and 2, which can be taken as a further indication of the formation of soluble intermediates of the oxidation process in agreement with

the presence of a Gerischer impedance in the spectra measured during decomposition of toluene.

Figure 8 shows XPS spectra of O1s, Pb4f, and Bi4f regions registered at the surface of pure and Bi–PbO₂ catalyst before the oxidation of toluene, whereas the

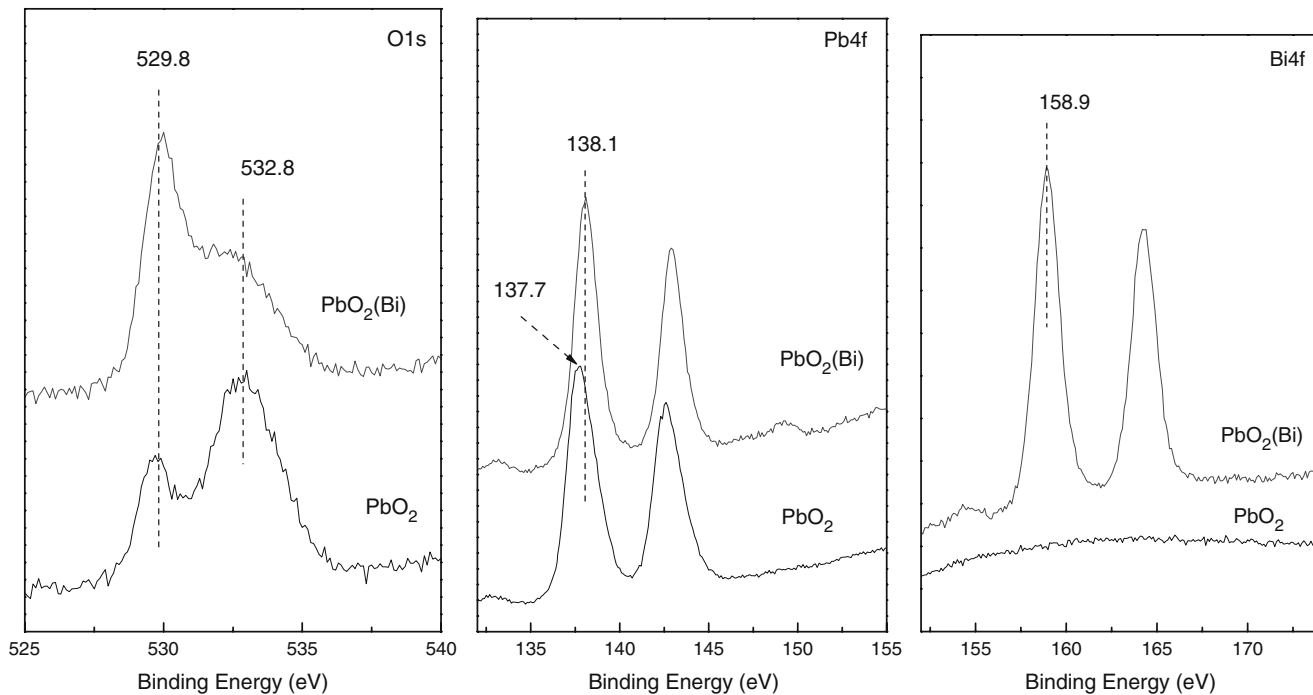


Fig. 8 XPS spectra of 1s, Pb4f, and Bi4f for pure and Bi-doped PbO₂ catalyst before the oxidation of 0.005 M toluene in 0.5 M H₂SO₄

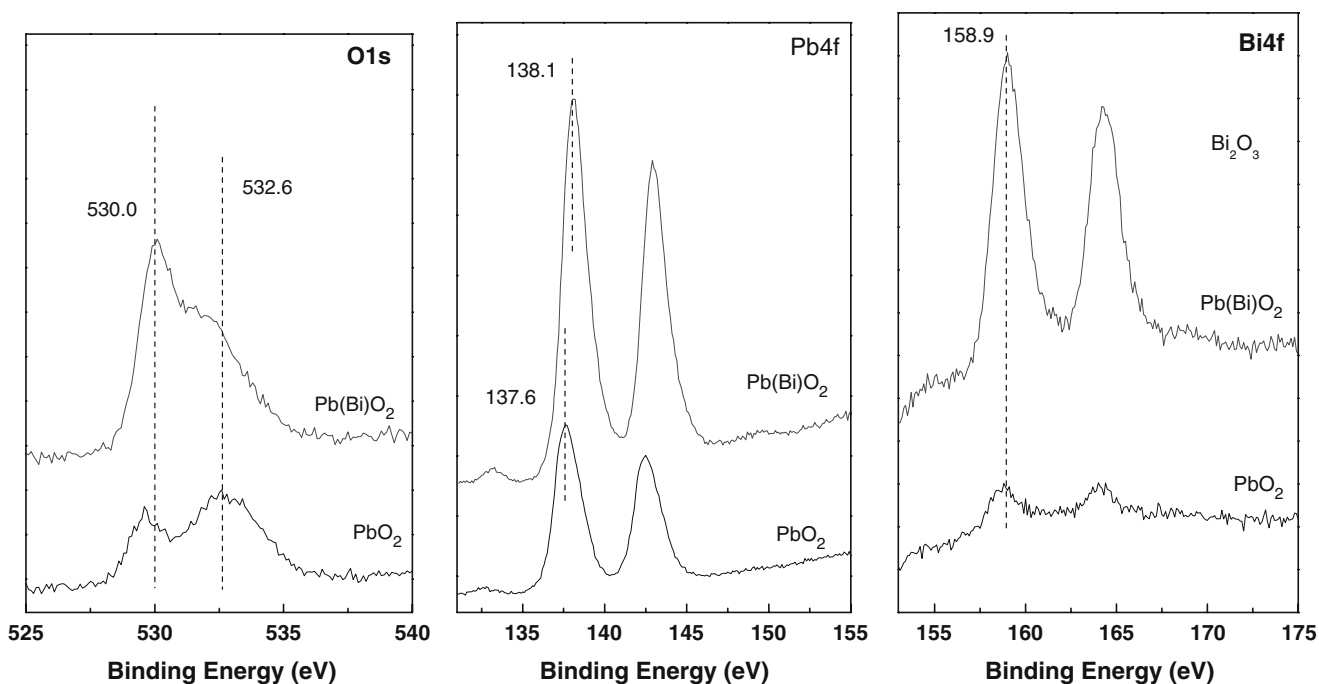


Fig. 9 XPS spectra of $\hat{1}1s$, $Pb4f$, and $Bi4f$ for pure and Bi-doped PbO_2 catalysts after oxidation of 0.005 M toluene in 0.5 M H_2SO_4 for 2 h at 1.35 and 1.40 V

respective spectra of the same catalysts after oxidation for 2 h at 1.35 and 1.40 V are presented in Fig. 9. The analysis of the spectra allows the conclusion that the stoichiometry of the oxide is very close to PbO_2 . For the Bi-doped oxide, the ratio of the surface concentrations of Bi and Pb is close to 1:1. In addition, the degree of hydration of the surface of the doped catalyst is lower than that of pure PbO_2 , which could be an indirect indication of the effective substitution of Pb with Bi. The chemical composition, stoichiometry, and valency states of the elements on the surface of the catalyst are preserved after toluene oxidation, which is an indication of its stability at high potentials in acidic solutions.

These conclusions were further substantiated by the X-ray diffractograms of the pure and Bi-doped PbO_2 catalysts presented in Fig. 10. In accordance with literature data, the predominant phase in the oxide layers is β - PbO . The grain size of this phase can be roughly estimated by applying Scherrer’s formula for the main peaks of β - PbO_2 . The estimated grain size is in the range of 10–20 nm and is about twice as small for the Bi-doped PbO_2 in comparison to the pure lead dioxide. Thus, the obtained catalysts are nanocrystalline, and the smaller grain size in the case of the Bi-doped PbO_2 probably leads to an increase in the true catalytic surface area and, hence, catalytic activity. A correlation between PbO_2 morphology and catalytic activity has been recently discussed by other authors [13].

According to a generalized mechanism for the oxidation of organics in the potential region of O_2 evolution [1–5],

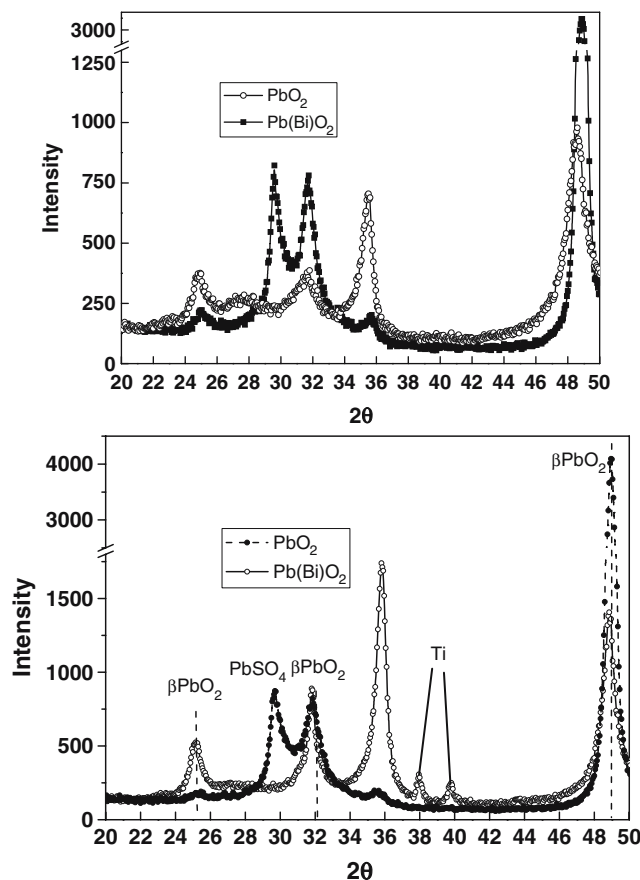
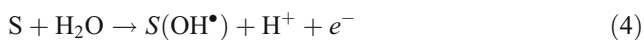
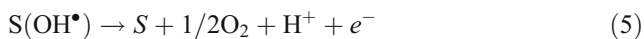


Fig. 10 X-ray diffractograms of the pure and Bi-doped PbO_2 catalysts before (above) and after (below) oxidation of 0.005 M toluene in 0.5 M H_2SO_4

the first step is the oxidation of water on the catalytic site [Bi-(V) site] on the PbO₂ surface (S)



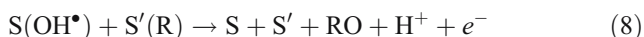
Then, the hydroxyl radicals may be either electrochemically oxidized to oxygen or assist the oxidation of the organic compound:



Several successive steps such as Eq. 6 can lead to the complete incineration of the organic compound with the liberation of CO₂. It has been more recently speculated [5] that the electro-catalytic benefit comes from pre-adsorption of the reactant species as described by:



Accordingly, the oxygen transfer step [reaction (6)] in this mechanism is expressed as:



It is apparent, from consideration of Eqs. 4 to 8, that anodic O transfer reactions can be expected to appear in the potential region corresponding to onset of oxygen evolution, as represented by reaction 5. The scheme described by Eqs. 4–8 is adapted to our case (oxidation of toluene in H₂SO₄ medium) in the following skeletal way:



Evidence for the presence of the adsorbed intermediate A_{ad} and the soluble intermediate B_{sol} has been found in the impedance spectra (see “Results”), whereas the existence of the soluble intermediate has been, to a certain extent, corroborated also by the UV spectrophotometric measurements.

Using standard electrochemical kinetics procedures, this scheme can be translated into a transfer function of the type described by Eq. 1. However, to estimate the kinetic parameters of all the electrochemically detectable reaction steps in a quantitative way, further investigations are needed to elucidate the chemical nature of the adsorbed intermediate A_{ad} and the soluble intermediate B_{sol}.

Conclusions

The results obtained at the present stage of this investigation clearly demonstrate that anodically electrodeposited mixed oxide coatings based on a PbO₂ matrix, doped with Bi ions to

form a mixed oxide phase, exhibit significant catalytic activity towards the oxidative destruction of harmful organics such as toluene. The catalytic activity has been estimated both from current vs potential and polarization resistance vs potential curves. Electrochemical impedance spectra measured during oxidation point to the presence of both adsorbed and soluble intermediates of the overall oxidation process. A tentative skeletal model of the process based on general considerations of the interaction of adsorbed water (oxidized to hydroxyl radicals) and the pre-adsorbed organic substances with the PbO₂ surface is proposed. It has been found to be in quantitative agreement with the electrochemical impedance spectra and in qualitative accordance to the UV spectroscopic results. The further confirmation of this model and the quantitative estimation of the kinetic parameters of the rate-determining steps await independent determination of the nature and quantity of the adsorbed intermediate species by spectroscopic methods.

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