ELECTROCHEMICAL OXIDATION OF TOLUENE DERIVATIVES 
ON Bi-DOPED PbO₂ IN SULPHURIC ACID SOLUTION

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ABSTRACT
In the present paper, the oxidative decomposition of toluene derivatives in sulphuric acid solution on Bi-PbO₂ layers deposited on Ti substrate is investigated by voltammetry and electrochemical impedance spectroscopy. Electrochemical impedance spectra measured during oxidation point to the presence of both adsorbed and soluble intermediates of the overall oxidation process. A transfer function including both heterogeneous and homogeneous chemical reactions besides the charge transfer step has been found to reproduce quantitatively the impedance spectra, and parameters related to the rates of the individual steps are estimated.

Keywords: bismuth-doped lead dioxide, toluene derivatives, electrooxidation, electrochemical impedance spectroscopy.

INTRODUCTION
Pollution of water is found to increase steadily due to further urbanization of the society and propagation of industry. Production, use and accordingly disposal of toxic organic chemicals have increased dramatically, and several of these compounds are resistant to biodegradation. Therefore, a major problem has been to treat wastewater in some way or another, before it is returned into the environment. Taking this into account, there is considerable interest in developing environmentally friendly methods to destroy aromatic hydrocarbons and their derivatives in order to avoid their accumulation in the wastewater streams released by the industry [1]. Technologies for wastewater treatment include physical, chemical, biological, and electrochemical processes. Biological processes cannot treat the high concentration of potentially harmful organics. Anodic oxidation of such impurities is considered to be a promising clean process, although it is subject to an important limitation, the selection of an anode material with high enough electrocatalytic activity [2, 3].

Basically, two types of electrodes have been widely investigated in recent years - metal oxide anodes, such as PbO₂, SnO₂, or RuO₂ [4-18], and boron-doped diamond electrodes [19-23]. Up to now, no universal opinion on the best electrocatalytic material exists. In order to be able to deterministically choose the best anodic material for a specific purpose, fundamental knowledge of the reaction mechanism of oxidative decomposition of organics is needed. Organic substances are thought to be destroyed and/or transformed by reactions with hydroxyl radicals formed from water discharge at the electrode surface under anodic polarisation [8-11]. The reactions taking place on the electrode are in fact oxygen-transfer reactions and may be summarised as follows. The first step is the oxidation of water on the catalytic site (e.g. Bi-(V) site on the PbO₂ surface, S)
\[ S + H_2O \rightarrow S(OH^+) + H^+ + e^- \]  

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

\[ S(OH^+) \rightarrow S + 0.5O_2 + H^+ + e^- \]

\[ R + S(OH^+) \rightarrow S + RO + H^+ + e^- \]

Several successive steps can lead to the complete incineration of the organic compound with the liberation of CO₂. It has been also speculated [11] that the electrocatalytic benefit comes from preadsorption of the reactant species as described by

\[ S' + R \rightarrow S'R \]

Accordingly, the oxygen transfer step in this mechanism is expressed as

\[ S'R + S(OH^+) \rightarrow S + S' + RO + H^+ + e^- \]

It is apparent, from consideration of eqs. (1) to (5), that anodic oxygen transfer reactions can be expected to appear in the potential region corresponding to onset of oxygen evolution.

In a previous paper [24] we successfully employed a combination between electrochemical impedance spectroscopy and UV-vis spectrophotometry to get an insight into the mechanism of generation of both adsorbed and soluble intermediate species during anodic oxidation of toluene in 0.5 M H₂SO₄ on Bi-doped PbO₂. The scheme expressed by reactions (1)-(5) has been adapted to that case in the following skeletal form

\[ C_6H_5CH_3_{ad} \xrightarrow{\text{charge transfer}} A_{ad} \xrightarrow{\text{desorption}} B \]

\[ \xrightarrow{\text{desorption}} B_{ad} \xrightarrow{\text{further oxidation}} CO_2 \]

As a continuation of our systematic investigation on electrochemical oxidation of aromatic hydrocarbons, in this paper we study oxidation of three toluene derivatives (p-bromotoluene, o-nitrotoluene and m-nitrotoluene) in 0.5 M H₂SO₄ on Bi-PbO₂ using voltammetric measurements and electrochemical impedance spectroscopy.

**EXPERIMENTAL**

The substrate material was pure Ti (99.9%), plates of which covered with acid-resistant lacquer and embedded in epoxy resin were used (exposed area 0.8 cm²). Their pretreatment consisted of mechanical abrasion with emery paper up to 1200 grade, followed by etching in 5% HF for 10 s. A conventional three-electrode cell featuring a Pt mesh counter electrode and a saturated calomel reference electrode (SCE) was employed for the electrodeposition procedure. The electrolytes for the anodic electrodeposition of the catalysts were 1 M HNO₃ + 0.5 M Pb(NO₃)₂ + 0.1% HF with the addition of 0.1 M Bi(NO₃)₃. No stirring of the solution was used. The electrodeposition of the Bi-doped PbO₂ was carried out as a two-step procedure. First, undoped PbO₂ was deposited at 1.65 V (vs. SCE) for typically 2 h, then the solution was changed to that containing the dopant ion and further deposition for 2 h at 1.7 V (vs. SCE) was carried out. Oxidation of toluene derivatives (1 mM solutions) was carried out in 0.5 M H₂SO₄ using the same cell but under continuous stirring of the solution in order to ensure reproducible hydrodynamic conditions.

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). Steady-state current vs. potential curves and impedance spectra at different potentials were registered (ac amplitude 10 mV, frequency range 10 mHz – 100 kHz). The linearity of the imped-

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*Fig. 1. Steady state current vs. potential curves of oxidation of 1 mM of toluene and its derivatives on Bi-PbO₂ in 0.5 M H₂SO₄. Dashed lines – Tafel fits to the data.*
RESULTS AND DISCUSSION

Fig. 1 shows the steady-state current vs. potential curves for the oxidation of toluene and the three derivatives on Bi-PbO$_2$ in 0.5 M H$_2$SO$_4$ solution. They were obtained by subtracting the currents obtained for the same material in blank 0.5 M H$_2$SO$_4$ as described earlier [24]. The values of the currents demonstrate that the catalytic activity of Bi-PbO$_2$ towards the electrooxidation of toluene and its derivatives is significant, in accordance to reports by earlier authors using voltammetric measurements [7]. In the low potential range (1.35 – 1.45 V), the current increases relatively slowly with potential, whereas a higher slope of the increase is observed at potentials exceeding 1.45 V. This feature is the most pronounced for toluene itself [24] and for m-nitrotoluene, whereas it is the least pronounced for p-bromotoluene, for which the largest oxidation currents were observed. For potentials higher than 1.45 V, the apparent Tafel slopes were close to 20 V$^{-1}$ for toluene and ortho-nitrotoluene, whereas the corre-

Fig. 2. Electrochemical impedance spectra of oxidation of 1 mM ortho-nitrotoluene in 0.5 M H$_2$SO$_4$. Points – experimental values, solid lines – best-fit calculation according to the transfer function described in the text.

Fig. 3. Electrochemical impedance spectra of oxidation of 1 mM meta-nitrotoluene in 0.5 M H$_2$SO$_4$. Points – experimental values, solid lines – best-fit calculation according to the transfer function.
Fig. 4. Electrochemical impedance spectra of oxidation of 1 mM para-bromotoluene in 0.5 M H₂SO₄. Points – experimental values, solid lines – best-fit calculation according to the transfer function.

Impedance spectra registered in the range of potentials in which oxidation of toluene derivatives proceeds on Bi-doped PbO₂ are presented in Figs. 2-4. Bode coordinates are used in order to emphasize the processes detected at both high and low frequencies. The impedance magnitude at low frequencies |Z|₁., which can be regarded as a first approximation of the total polarisation resistance increases with potential, the feature being the most pronounced for p-bromotoluene (Fig. 4). The values of |Z|₁. are the smallest for p-bromotoluene and the largest for m-nitrotoluene, in certain analogy to the current vs. potential curves. The values of impedance at ca. 100 Hz, that can be roughly taken as a measure of the charge transfer resistance, are also the smallest for p-bromotoluene and the largest for m-nitrotoluene (Figs 2-4). The phase angle vs. frequency curves depicted in Figs 2-4 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 derivatives. 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, as found previously for the oxidation of toluene [24].

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 derivatives [24]:

\[ Z = R_{el} + \frac{1}{Z_f + \frac{1}{\frac{1}{R_i} + \frac{1}{j\omega C_a + \frac{1}{R_s + Z_G}}}} \]  

where \( R_{el} \) is the resistance of the electrolyte, \( R_i \) is the charge transfer resistance, \( R_s \) is the resistance of the adsorption process, and \( C_a \) is the adsorption pseudocapacitance. In this function, \( Z_f \) is the Young impedance describing the electric properties of the TiO₂ layer [25]:

\[ Z_f = \frac{P}{j\omega C} \ln \left( \frac{1 + j\omega \rho a \varepsilon \varepsilon_0 e^{-\frac{1}{\rho a}}}{1 + j\omega \rho a \varepsilon \varepsilon_0} \right) \]  

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 electric properties of the anodic oxide on Ti. In the Young impedance function (7), \( C \) is the layer capacitance, \( P \) is the relative permeation depth of defects in this layer, \( \rho_a \) is the resistivity at the interface.
at which such defects are generated, \( \varepsilon \) is the dielectric constant of the oxide layer, \( \varepsilon_0 \) is the permittivity of free space and \( \omega \) is the angular frequency of the ac signal.

Further, in the transfer function described by equation (6), \( Z_\infty \) stands for the so-called Gerischer impedance [26] describing the frequency response of a homogeneous chemical reaction that proceeds after the charge transfer step:

\[
Z_\infty = \frac{1}{Y_0} \left( \sqrt{\frac{\omega^2 + k^2}{\omega^2 + k^2}} - j \sqrt{\frac{\omega^2 + k^2}{\omega^2 + k^2}} \right)
\]  \hspace{1cm} (8)

where \( Y_0 = \frac{(nF)^2 \varepsilon \sqrt{Dk}}{RT} \), \( \overline{c} \) 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 (6 - 8) are presented in Figs 2-4 with solid lines and demonstrate that the proposed function can satisfactorily account for the experimental data in the whole investigated range of potentials for the three studied toluene derivatives. Its validity has been earlier demonstrated also for the oxidation of toluene on Bi-PbO$_2$ in 0.5 M H$_2$SO$_4$ [24]. The main parameters extracted from the fitting procedure are collected in Fig. 5. The following conclusions can be drawn from the values of the parameter estimates as depending on potential and the derivative type:

- The capacitance of the TiO$_2$ layer stays 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 (Fig. 5a). On the other hand, the values of this capacitance for the three toluene derivatives are much higher than that for toluene (data from Ref. 24 presented for comparison), which may indicate that when the derivatives are adsorbed on the surface, they alter significantly the electric properties of the oxide surface. As this capacitance may also be regarded as a sum of the capacitances of the depletion layer of the TiO$_2$ semiconductor in contact with the conductive PbO$_2$ overlayer and the Helmholtz capacitance at the PbO$_2$/electrolyte interface, it can be tentatively concluded that in the case of adsorption of the toluene derivatives the capacitance C is dominated by the double-layer contribution.

- The charge transfer resistance is by far the smallest for p-bromotoluene, and the largest for toluene itself (Fig. 5b). It preserves more or less constant values with increasing potential, indicating that the charge transfer reaction is probably controlled by migration of electronic defects through the TiO$_2$ sublayer.

- The pseudocapacitance of the adsorbed intermediate, C$_p$, exhibits relatively large values and increases with potential for toluene and the two nitro-derivatives (Fig. 5c). Conversely, its values stay low and decrease with potential in the case of p-bromotoluene. Combining this with the smallest value of the charge transfer resistance in the case of this compound, it can be proposed that the adsorbed intermediate is much more stable in this case and maybe forms a 2D condensed layer at the PbO$_2$ surface. This hypothesis is to a certain extent corroborated by the fact that the desorption resistance $R_s$ for p-bromotoluene exhibits a much weaker potential dependence when compared to the other studied derivatives (Fig. 5d).

- Both parameters of the Gerischer impedance ($Y_s$ and $k$) increase quasi-exponentially with potential indicating that charge transfer determines to a certain extent the rate of the homogeneous reaction (Figs 5e-f). The values of $Y_s$ are the smallest for toluene and the largest for p-bromotoluene, indicating that the equilibrium concentration of the reactant is the largest in the latter case (the values of the formal rate constant $k$ do not differ significantly between the studied compounds indicating close values of the exchange reaction rate).

**CONCLUSIONS**

The results of this investigation clearly demonstrate that anodically electrodeposited mixed oxide coatings based on a PbO$_2$ matrix, doped with Bi ions to form a mixed oxide phase, exhibit significant catalytic activity towards the electrooxidation of toluene derivatives. 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 (oxidised to hydroxyl radicals) and the preadsorbed organic substances with the PbO$_2$ surface is proposed.

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**REFERENCES**