

Express-method for Estimation of Electrocatalytic Activity of Oxide Films toward Oxygen Transfer Reactions

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Abstract Oxidation catalysis of organic substances has attracted special attention in recent years due to of their high industrial significance in green and energy chemistry. The implementation of a transition metal-based catalyst in combination with oxygen is an alternative to the traditional procedures. This study justifies the application of amperometric response 'in situ' for estimation of the electrocatalytic activity of metal oxide films, which are known to be promising for oxygen transfer processes. The reaction of electrooxidation of Mn^{2+} ions may be termed as a 'marker' for oxygen transfer reactions due to its kinetic features, such as proportionality between the current density and the surface concentration of $\bullet\text{OH}$ -radicals. The relative parameter, k_{ox} , has been offered for estimation of the oxidizing capacity of an anode material toward oxygen transfer reaction in reference to platinum oxidizing capacity. k_{ox} value is automatically calculated exactly during electroplating of MnO_x as a ratio of the current density of $\text{Mn}^{2+} + 2\text{H}_2\text{O} - 2e \rightarrow \text{MnO}_2 + 4\text{H}^+$ reaction on the tested surface to the current density of this reaction on Pt surface. The developed method was tested during the investigation of catalytic activity of MnO_x films for electrooxidation of glucose. The parameter k_{ox} was calculated for other anode materials and was analyzed. The application of the new method allows estimating and comparing the catalytic performance toward oxygen transfer reactions of anode materials or of the same material in different modifications, such as nano particles, composites, different compositions etc. The pre-test reduces manifold the time spent for determination of oxidizing capacity of oxides.

Keywords Manganese Oxides, Electrocatalytic Oxidation, Oxygen Transfer Reactions

1. Introduction

Oxidation reactions play an important role in chemical industrial processes. However, the processes, involving traditional mostly toxic oxidant and by-products, cause high levels of environmental pollution. The implementation of a transition metal-based catalyst in combination with oxygen is an alternative to the traditional procedures [1-6]. Such systems are an essential condition for implementation of sustainable green chemical processes. Thus, the development of these systems is a driving force for fabrication of novel and efficient catalytic materials. The basic feature of catalysts is the ability to generate and adsorb onto the surface the active oxygen particles, such as O^{2-} , $\text{O}^\cdot$, $\text{O}_2^\cdot$, $\bullet\text{OH}$ etc. Transition metal based catalysts are the promising material for the practical oxidation of organic substances due to their high efficiency, stability, low cost and convenient synthesis. Therefore, it is important to understand the properties of transition metal oxides and to improve catalytic activity, basing on their features.

Recently, manganese dioxide has received much attention. MnO_2 has been widely used in catalysis and molecular adsorption [7-13]. However, the application of MnO_2 was restricted by its poor electrical conductivity. Therefore, the synthesis of GR/ MnO_2 or graphene/ MnO_2 composites has been proposed as an effective solution to this problem [14-17]. We have noted that MnO_2 is synthesized most frequently by hydrothermal or chemical method. Scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR) are usually used to investigate the structure and morphologies of the composites. However, these analytical methods do not provide information about the ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ forms in the solid phase of MnO_x , which

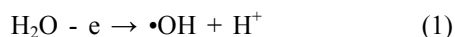
strongly affects the catalytic activity of the material. Compared to other methods of synthesis, electrochemical plating method allows us to obtain low cost oxide films of a fixed composition. Electroplating is a simple and replicable method, which is particularly important in industry.

The electrocatalytic activity of materials is generally investigated, using the common procedure: the test substance is oxidized at the electrode under long-term cyclic voltammetry and this process is accompanied by sampling and quantitative analysis of samples [18]. However, it is difficult to determine the optimal composition of a metal oxide film, because the composition and the structure of the film can vary widely.

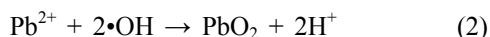
From our point of view, the above-mentioned long-term procedure of direct measurement of the investigated reagent oxidation rate at the surface of the catalyst can be changed for express-estimation of the catalyst for aerobic oxidation of organic compounds oxidizing capacity. The proposed method is based on the kinetic features of manganese dioxide film formation mechanism at the non-native surface.

It is considered that Pb^{2+} and Mn^{2+} cations are oxidized at high anodic applied potential due to interaction mainly with adsorbed OH-radicals, produced by the water-splitting reaction [19, 20]. The overall process of oxidation of Pb^{2+} and Mn^{2+} cations is presented schematically as follows:

Primary process:



Subsidiary process:



As it can be seen from the reactions (2) and (3), the rate of Pb^{2+} and Mn^{2+} cations oxidation process is proportional to the surface concentration of OH-radicals. Therefore, the oxidizing capacity of the anode material can be evaluated by the rate of the reaction (2) or (3) at the surface of this material. So we use current density of MnO_2 or PbO_2 electroplating as the indicator of electrocatalytic activity of an electroplated material toward oxygen transfer reactions. Accordingly, the reactions (2) or (3) may be termed as "markers" for material surfaces which are capable of adsorbing active oxygenated particles.

Thus, in this paper we focus our attention on MnO_2 , because the electrodes with active layer of manganese oxides are considered as an advanced, low cost and non-toxic electrocatalyst.

Our suggested express-estimation of electrocatalytic activity of a catalyst method was tested by electrooxidation of glucose. Glucose is a very stable compound, which makes it difficult to be oxidized electrochemically. Therefore, catalysts are important for using the glucose in fuel cells and pharmaceutical industry.

2. Materials and Methods

2.1. Reagents and Materials

All the electrolytes, used in this study, were prepared from AR grade $\text{Pb}(\text{NO}_3)_2$, MnSO_4 , Na_2SO_4 and concentrated H_2SO_4 , using double distilled water. The concentrations of electrolytes were in the range of 0,02-0,05M MnSO_4 and 0,5M Na_2SO_4 , pH was in the range of 1-4; 0,02M $\text{Pb}(\text{NO}_3)_2$. Glucose concentration was 25mM and 1M NaOH.

2.2. Kinetic Measurements

Electrochemical experiments were carried out on the PI-50-1 Potentiostat-Galvanostat electrochemical workstation connected to the programmer PR-8 with a conventional three-electrode system. As a working electrode we used:

- Pt wire of fixed area ($0,13\text{cm}^2$), sealed into teflon. Before measurement the Pt electrode was treated with a solution containing H_2SO_4 and H_2O_2 (2:1) during 3 minutes and was washed in water.
- Ti plate was treated with ethanedioic acid (10%) at 90°C during 1 hour and was washed in water. The area of Ti electrode was limited with teflon tape ($0,2\text{cm}^2$).
- PbO_2 electrode was prepared via electroplating from $\text{Pb}(\text{II})$ nitrate on the Pt electrode ($0,13\text{cm}^2$).
- MnO_2 electrode was prepared via electroplating from $\text{Mn}(\text{II})$ sulfate on the Pt electrode ($0,13\text{cm}^2$).

As a counter electrode Pt (2cm^2) and as a reference electrode Ag/AgCl electrode (saturated with KCl) was used.

Anodic electrodeposition of MnO_2 was performed at a constant potential 1,4V at 40°C from $\text{Mn}(\text{II})$ sulfate.

Anodic electrodeposition of PbO_2 was performed at a constant potential 1,75V at 25°C from $\text{Pb}(\text{II})$ nitrate.

The obtained data were recorded on the computer using a digital recorder.

2.3. Measurement of the Rate of Glucose Oxidation Reaction

Glucose oxidation process was performed potentiostatically ($E=1,4\text{ V}$) at 40°C with intensive mixing. Graphite, modified by MnO_2 ($0,8\text{cm}^2$), was used as an anode.

Glucose concentration in the solution was measured every 2 min using glucose biosensor at aliquot temperature of 25°C , relative error is 0,5%.

3. Results

Fig.1 (curve 1) shows a typical amperometric response

of Pt electrode in MnSO_4 solution. Experimental amperometric response curves could be divided into three regions:

(I and III) the first and third region is monotone-decreasing relations, following equation for the electrode process controlled by linear diffusion [21] (Fig.2);

(II) at the second region the increase of the curve was observed;

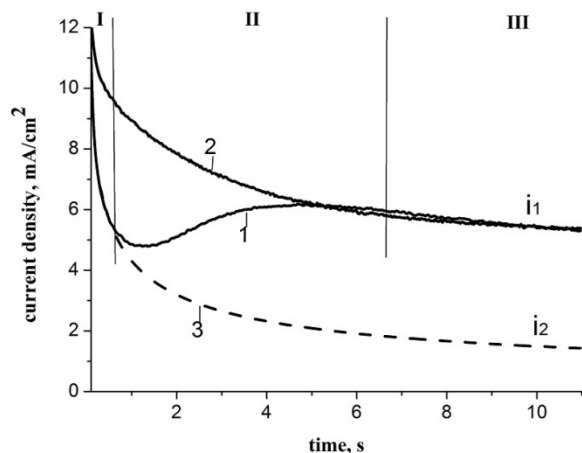


Figure 1. Amperometric response of Pt electrode in 0.05M MnSO_4 and 0.5M Na_2SO_4 , pH 1 at 1.4V; 2 - amperometric response of MnO_x electrode in 0.05M MnSO_4 and 0.5M Na_2SO_4 , pH 1 at 1.4V; 3 - calculated amperometric response of PtO_y electrode (extrapolation of region (I) of curve1).

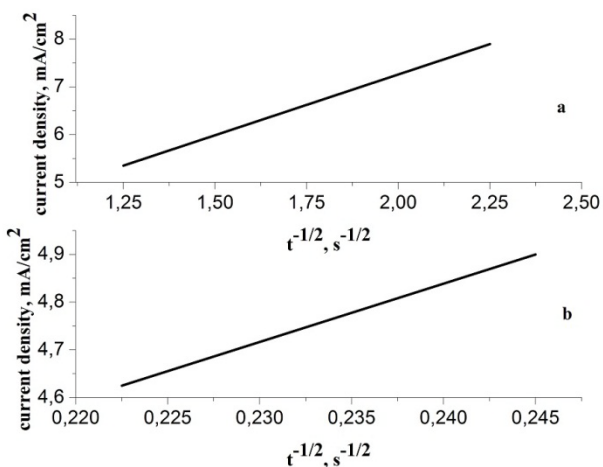


Figure 2. Plot of current density vs. parameter $t^{-1/2}$: a - in the region (I), b - in the region (III) (Fig.1, curve1).

Such kinds of amperometric response curves are typical for processes with products which can catalyze the main reaction. For the studied reaction (3) this product is MnO_2 . The formed MnO_2 crystals on the Pt surface increase the electrode area and change its adsorbing capacity. Therefore, during MnO_2 electroplating at the non-native surface (in our case it is Pt) the concentration of OH-radicals, adsorbed on the anode surface, varies. This implies that the rate of reaction (3) varies too.

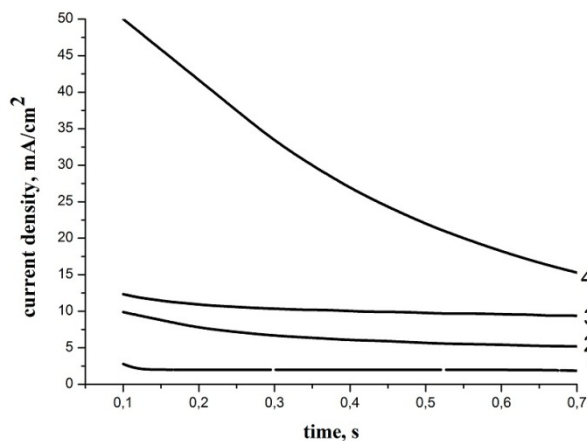


Figure 3. Amperometric response of 1 – Ti anode; 2 – Pt anode; 3 – MnO_2 anode; 4 – PbO_2 anode in 0,05 M MnSO_4 and 0,5 M Na_2SO_4 , pH 1 at 1,4 V (amperometric response of Ti anode at 1,5 V)

If the nature of OH-radicals adsorption process on manganese oxides changed slightly as compared to the platinum surface, we would have a typical amperometric response curve. The comparison of the initial region of amperometric response curves of different electrodes (Fig.3) suggests that OH-radicals concentration on the surface of the MnO_2 -film is larger than on the Pt surface, and on the Pt surface OH-radicals concentration is larger than on the Ti surface. The maximum values of current were obtained for the PbO_2 -film. These data correspond to the studies of oxidizing power of PbO_2 -films [22].

Consequently, the transition region (II) of amperometric response curve (Fig.1, curve 1) corresponds to the gradual coating of platinum surface by manganese oxide crystals until full coverage. This process is revealed by anode current increasing. The region (III) (Fig.1, curve1) corresponds to the process of Mn^{2+} oxidation on the MnO_2 -film surface.

This hypothesis has been confirmed by comparison of amperometric response curve of MnO_x electrode and amperometric response curve of non-native electrode. Fig.1 shows the overlay of curves 1 and 2 in the region (III).

4. Discussion

Our conception of the kinetic features of manganese dioxide electrodeposition on metal oxide surface is the basis for the method of estimation of catalytic activity of metal oxide film towards anode oxygen transfer reactions. Using the parameters of diffusion equation of the region (I) of experimental amperometric response curve (Fig.1, curve1), the calculated amperometric response curve of PtO_y in MnSO_4 solution (Fig.1, curve 3) has been received by applying extrapolation method. The increase of OH-radicals concentration on the MnO_x surface, compared to PtO_y surface, could be evaluated by the ratio of current density of experimental CA curve of MnO_x (i_1) (Fig.1,

curve 1, region (III)) to corresponding current density of the calculated amperometric response curve of PtO_y (i_2) (Fig.1, curve4) at fixed moment:

$$k_{ox} = \frac{i_1}{i_2} = \frac{[\text{OH}_{ad}](\text{MeO}_x)}{[\text{OH}_{ad}](\text{PtO}_y)} \quad (4)$$

Generally, $[\text{OH}_{ad}]$ could be estimated directly from the value of current density i_1 , but from our point of view using relative values with platinum as a standard is more preferable.

This method was applied for investigation of the effect of MnO_x film composition on the surface capacity to adsorb OH-radicals, as well as of catalytic performance of anode material. The presence of $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox couple in the solid phase of MnO_x has been used as an explanation for special properties of MnO_x -films by authors [23-25]. The appearance of the redox couple can be explained by the possibility of co-precipitation of MnO_2 and Mn_2O_3 oxides. Therefore, the value of x for MnO_x is in the range $1,5 \leq x \leq 2,0$ and also has to be in accordance with the concentration of oxides.

K.Vetter found the relation between the composition of electroplated MnO_x film and pH of the solution, together with Mn^{2+} concentration [26]. We used $x=f(\text{pH})$ dependence for electroplating MnO_x films of fixed composition on platinum. Precipitations were carried out in solutions with different pH at a constant potential of 1,4V, corresponding to the anode peak on CV curve. During electroplating of MnO_x , k_{ox} value was calculated automatically, applying the suggested approach. Thus, the effect of MnO_x film composition on the k_{ox} , as well as the rate of oxidizing capacity of anode material, was evaluated. As it is shown in Fig.4 (curve1), $k_{ox}=f(x)$ dependence demonstrates the extreme character and the peak has been obtained at $x=1,895$. Using the system of equations $x=a*1,5+b*2,0$ and $a+b=1$, where a - mole fraction of Mn_2O_3 , b - mole fraction of MnO_2 , qualitative and quantitative composition of sediment $\text{MnO}_{1,895}$ was calculated.

Thus, the film consisting of 21% Mn_2O_3 and 79% MnO_2 has the highest surface capacity to adsorb atomic oxygen.

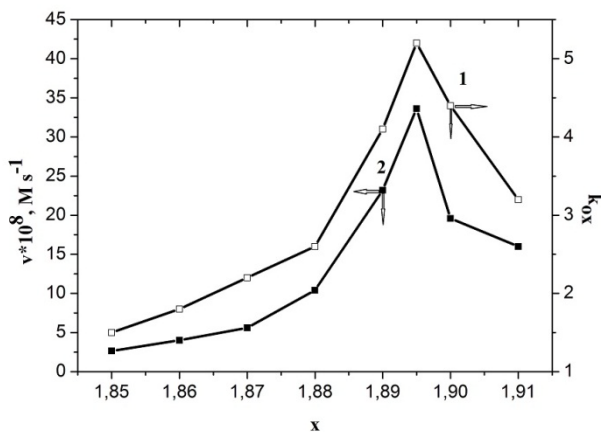


Figure 4. 1-plot of calculated k_{ox} value vs. composition of MnO_x film; 2-plot of glucose oxidation rate vs. composition of MnO_x film

The study of kinetic features of glucose oxidation at MnO_2 -anodes was used for estimation of the catalytic effect of MnO_2 -films. The rate of glucose oxidation in alkaline solution was evaluated by the common procedure, which includes sampling and quantitative analysis of samples [27-29].

Fig.4 (curve 2) shows the extreme character of dependence of glucose oxidation rate on anode film composition. It should also be noted that curve 1 corresponds to curve 2 as it was expected. This fact can be considered as a sufficient reason for using k_{ox} value for the estimation of electrocatalytic activity of electrolytic MnO_x films toward oxygen transfer reaction.

Table 1. Values of k_{ox} , calculated for different anode materials.

Anode material	PtO_x	TiO_x	PbO_x	$\text{MnO}_{1,85}$	$\text{MnO}_{1,895}$
k_{ox}	1,0	0,3	5,7	1,5	5,1

The parameter k_{ox} for different anode materials was calculated according to the equation (4) on the basis of amperometric responses, reported in Fig.3. The results are shown in Table 1. It had become clear that the relative parameter k_{ox} allows estimating and comparing the catalytic performance toward oxygen transfer reaction of anode materials or of the same material in different modifications, such as nano particles, composites, different compositions etc.

It should be noted that not only OH-radicals, but also such oxidizing agents as atomic oxygen, molecular oxygen, ozone and superoxides are produced by the water-splitting reaction at the anode surface. Thus depending on substance the nature of various mechanisms of oxidation process can be implemented at the anode. These mechanisms include direct electrooxidation of substance at the electrode.

Therefore, the results of amperometric response express-test have to be confirmed by kinetic investigation of the real object. However, the pre-test reduces manifold the time spent for determination of the catalyst tailors composition.

5. Conclusions

The interrelation between the amount of OH-radicals and the current density of $\text{Mn}^{2+} + 2\text{H}_2\text{O} - 2e \rightarrow \text{MnO}_2 + 4\text{H}^+$ reaction, including the intermediate stage $\text{Mn}^{2+} + 2\text{OH}^- \rightarrow \text{MnO}_2 + 2\text{H}^+$, was used in the development of a new method of estimation of electrocatalytic activity of anode material. Therefore, the reaction of electrooxidation of Mn^{2+} ions in this context may be termed as a "marker" for oxygen transfer reactions. We suggested the application of the relative parameter – k_{ox} , i.e. the ratio between the current density of this reaction on an oxide surface and the current density on Pt surface at a certain point of time. The developed method was tested during the study of catalytic activity of MnO_x films for electrooxidation of glucose. The

effect of MnO_x film composition on k_{ox} value was shown. In accordance with experimental $k_{ox}=f(x)$ dependence, the curve demonstrated its peak, obtained at $x=1.895$, which corresponded to the anode film, consisting of 21% Mn_2O_3 and 79% MnO_2 .

This composition of a catalytic film performs the highest rate of glucose electrooxidation, as well as the maximum of the obtained values of the parameter k_{ox} . Thus, we observe the correlation of the results of the traditional method of the catalyst estimation and the express-test, proposed in our study.

We suggest the most rapid technique of estimation of catalytic power of oxides toward oxygen transfer reactions for the present time.

The parameter k_{ox} was calculated for other anode materials. The obtained results corresponded to the intended ones.

The application of the new method allows estimating and comparing the catalytic performance toward oxygen transfer reactions of different kinds of oxides, including their modifications.

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