Electrochemical behavior of a composite layer of RuO$_2$ and NiO deposited on nickel and titanium electrodes has been studied in acidic, neutral and alkaline media with and without chloride. Cyclic voltammetry was used for the electrochemical studies, whereas the methods of X-ray electron spectroscopy and scanning electron microscopy were employed for the investigation of the oxide layer composition and surface morphology.

It has been found that the composite layer of RuO$_2$ and NiO deposited thermally on titanium electrode has a synergetic catalytic effect on the evolution process of O$_2$ in both strongly acidic and strongly alkaline media.

It has been shown that Ti/RuO$_2$·NiO electrode can be used for obtaining pure oxygen by electrolyzing sea water alkalized to pH $\geq 4$.

**Key words**: oxygen evolution, ruthenium, nickel, oxide electrode

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**INTRODUCTION**

Oxygen evolution reaction (OER) taking place on the surfaces of RuO$_2$, IrO$_2$, oxides of iron subfamily metals and other oxides is the object of continuous investigations due to its importance in such areas as seawater electrolysis and energy conversion technologies [1–8]. Researches are being carried out in order to achieve the conditions that would make the process of O$_2$ evolution technological and as facile as possible. As regards seawater electrolysis, the main challenge is to ensure the purity of oxygen gas preventing the possible contamination with Cl$_2$. Izumiya et al. have reported [9] that in the case of Ti / IrO$_2$ / MnO$_2$ electrode in a slightly alkaline medium, O$_2$ yield can be increased from $\sim 70\%$ to $\sim 90\%$ by introducing Mo oxides into the oxide layer. Among the best known catalysts for OER are ruthenium and iridium dioxides (RuO$_2$ and IrO$_2$) and Co and Ni oxides [2]. Mixtures of Ni and Co oxides of NiCo$_2$O$_4$ or CoNi$_2$O$_4$ type are used in alkaline media [3–6], but they are weaker depolarizers of OER as compared to RuO$_2$. On the other hand, RuO$_2$ is more expensive and not sufficiently stable in alkaline and acidic media due to the possible oxidation to soluble Ru(VI), Ru(VII) or volatile Ru(VIII) compounds.

In the present work we have attempted to form a layer of composite RuO$_2$ and NiO on nickel and titanium substrates with the purpose to evaluate its electrochemical and catalytic properties for O$_2$ evolution reaction. Electrocatalytic properties of such mixed oxide in H$_2$ evolution reaction as well as the possibilities of its application for electrochemical supercapacitors have been investigated in [10–12].

**EXPERIMENTAL**

**Synthesis of mixed oxide layer**

The layer of the composite Ru and Ni oxides on titanium substrate was formed as follows: the Ti electrode was etched for 2 min in hot (80 °C) diluted H$_2$SO$_4$ (1 : 1), washed with water and blotted with filter paper. Then a layer of a solution containing RuOHCl$_3$, NiCl$_2$·6H$_2$O, HCl, isopropanol and water (pH $\approx 0$) was painted onto the Ti electrode and dried for several minutes at 65–80 °C. The molar ratio of Ru and Ni in the solution was 1 : 1. Such painting and drying procedure was performed for 5 times and then the electrode was heated additionally for 1 h at 400 °C in air. Approximate thickness of RuO$_2$·NiO layer was $\sim 0.5$ µm.

The layer of the composite Ru and Ni oxides on nickel substrate was formed as follows: the nickel electrode was degreased with a fine-grained pulp of MgO + Ca(OH)$_2$, polished with water-proof emery paper, washed and blotted with filter paper. Immediately after this a layer of the solution containing RuOHCl$_3$, HCl, isopropanol and water (pH $\approx 0$) was painted onto the nickel surface, dried at $\sim 80$ °C and heated for 5 min at 400 °C. Such procedure was performed for 3 times.

Chemicals of analytical grade and triply distilled water were used to prepare the solutions.
Electrochemical measurements

The voltammetric measurements were performed using a PI-50–1.1 potentiostat with a PR-8 programming device (Russia) connected to a personal computer. A conventional ~25 cm$^3$ glass cell with separate working, counter and reference electrode compartments was used. A pure Pt (99.99%) plate served as the counter electrode. Hydrogen electrode in a working solution (RHE) was used as the reference electrode. The potential values in the text are referred to RHE scale. The relationship between the two scales is expressed in the following way: $E_{\text{RHE}} = E_{\text{SHE}} - 0.059 \ \text{pH}$. All the current density values given in the text refer to the apparent area of the working electrode, i.e. 1.0 cm$^2$. All the experiments were carried out at room temperature (20 °C).

XPS and SEM measurements

The composition of the composite oxide coatings was analyzed by X-ray photoelectron spectroscopy. The spectra were recorded with a spectrometer “ESCALAB MK II” (VG Scientific, Great Britain) using X-radiation of MgK$_\alpha$ (1253.6 eV, pass energy of 20 eV). The spectrometer had a base pressure of 5 · 10$^{-8}$ Torr in the analyzer chamber and 2 · 10$^{-8}$ Torr in the sample preparation chamber, where Ar$^+$ ion bombardment was performed. For sputter etching, the argon gas pressure was maintained at 6 · 10$^{-5}$ Torr and the ion gun was operated at 2 kV. The approximate rate of the oxide phase etching was 0.1–0.2 nm min$^{-1}$ µA$^{-1}$.

Quantitative elemental analysis was performed by estimating the peak areas and taking into account the empirical sensitivity factors for each element [13], and then the spectra recorded were compared with the standard spectra [14, 15]. The binding energies were calibrated with respect to the C 1s electron peak at 284.6 eV due to the residual pump oil on the sample surface. Not less than 5 spectra were recorded for every element. The maximum accuracy of the method was 0.1%. Standard and experimental binding energy values for nickel and ruthenium compounds are given in Table 1 [14, 15]. A standard program was used for data processing (XPS spectra were treated with a Shirley-type background subtraction and fitted with mixed Gaussian–Lorentzian functions).

Surface morphology of the composite Ru and Ni oxide electrodes was studied using a scanning electron microscope EVO 50 EP (Carl Zeiss SMT AG, Germany) with energy dispersion and wave dispersion X-ray spectrometers (Oxford, UK).

Table: Standard binding energies of nickel and ruthenium compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ni 2p$^{3/2}$</th>
<th>O 1s</th>
<th>Ru 3d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>852.5 ± 0.1</td>
<td>852.6</td>
<td></td>
</tr>
<tr>
<td>Ni(OH)$_2$</td>
<td>856.0 ± 0.2</td>
<td>855.8</td>
<td>530.8–531.7</td>
</tr>
<tr>
<td>NiO</td>
<td>853.3–854.4</td>
<td>854.1</td>
<td>529.3–530.7</td>
</tr>
<tr>
<td>Ru</td>
<td></td>
<td></td>
<td>280.0 ± 0.1</td>
</tr>
<tr>
<td>RuO$_2$</td>
<td>529.4</td>
<td>529.3</td>
<td>280.9 ± 0.1</td>
</tr>
<tr>
<td>RuO$_3$</td>
<td>530.7</td>
<td>530.7</td>
<td>282.5</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

XPS spectra characterizing the surface state of the composite oxide layer on Ti substrate as-deposited and after argon etching (20 µA, 30 s), are presented in Figs. 1a and 1b, respectively. The analysis of the spectra as well as standard and experimental binding energy values given in Table 1 shows that the main components of the as-deposited oxide layer are RuO$_2$, RuO$_3$, Ni(OH)$_2$, NiO and NiCl$_2$ (Fig. 1 a). No RuO$_3$ was found on the electrode surface after the removal of a thin surface layer (~2 nm) by means of argon etching (Fig. 1 b), whereas some of the metallic Ru and Ni was detected.

Fig. 2 shows a SEM image of RuO$_2$·NiO coating on the titanium substrate. The micrograph reveals a cracked-mood-looking appearance of the electrode surface, which is typical of thermally formed RuO$_2$ oxide layers on titanium substrate [7, 16].

Fig. 3 illustrates the voltammetric behavior of the composite RuO$_2$·NiO layer on nickel in the solutions of 0.5 M H$_2$SO$_4$ and 1 M KOH. A comparison of curves 1 and 2 with the voltammetric response of pure nickel electrode (curve 3) shows that the addition of RuO$_2$ to the surface oxide layer on the nickel electrode significantly depolarizes the oxygen evolution process. The positive effect of RuO$_2$ is especially pronounced at high anodic current densities. Since nickel is not sufficiently chemically inert, the layer of the composite oxides was formed on titanium substrate, which does not suffer from this disadvantage. A comparison of curve 1 in Fig. 4 with literature data for Ti / RuO$_2$·TiO$_2$ electrode [7] (Fig. 4, curve 2) shows that in the case of the strongly acidic solution (0.5 M H$_2$SO$_4$), the influence of NiO on the rate of OER is insignificant – up to ~50 mA cm$^{-2}$, whereas at higher anodic current densities it becomes evident as the process is depolarized by ~50 mV. The average value of the slope $dE / dlgi$ for curve 1 (Fig. 4) is close to ~60 mV. Similar values of $dE / dlgi$ have been reported in literature [7] for the range of low anodic current densities, i.e. 20–30 mA cm$^{-2}$, whereas at higher values of $i_a$, $dE / dlgi$ increases considerably. In slightly acidic and neutral media (Fig. 4, curves 3 and 4), the oxygen evolution on the Ti / RuO$_2$·NiO electrode becomes significantly hindered. The beginning of the process shifts from 1.4 V to ~1.8 V (Fig. 4, curve 3) and even to ~2.0 V (Fig. 4, curve 4) in a slightly acidic and neutral solution of K$_2$SO$_4$, respectively. The oxygen evolution process in the case of the positive going part of the cycle is relatively easier, i.e. takes place at lower potentials than in the case of negative going part. This is related to the oxidation of NiO to NiO$_2$, [17] and the passivation of the electrode surface, as discussed in [18]. NiO$_2$, presumably suppresses the electrocatalytic effect of RuO$_2$, so the use of the Ti / RuO$_2$·NiO anode for OER in slightly acidic and neutral media makes no sense. In the case of the strongly acidic medium, NiO is not stable on the electrode surface [17]. As it has been mentioned above, the presence of NiO in the surface oxide layer depolarizes the process of oxygen.

Fig. 4. Cyclic voltammograms of Ti / RuO$_2$·NiO electrode in: 1 – 0.5 M H$_2$SO$_4$, 2 – literature data for Ti / RuO$_2$·TiO$_2$ in 0.5 M Na$_2$SO$_4$, pH = 2, 60 °C [7], 3 – 0.5 M K$_2$SO$_4$ + 0.001 M H$_2$SO$_4$, 4 – 0.5 M K$_2$SO$_4$ (pH = 5.5); $v = 50$ mV s$^{-1}$, 20 °C

Fig. 5. Cyclic voltammograms of Ti / RuO$_2$·NiO electrode in: 1 – 1 M KOH, 2 – 4 – 0.5 M K$_2$SO$_4$ + 0.01 M KOH (4 – in stirred solution); $v = 50$ mV s$^{-1}$, 20 °C
evolution; however, NiO should not be sufficiently stable under such conditions.

In a strongly alkaline medium, the layer of the composite RuO\(_2\)–NiO on Ti substrate is very efficient from the catalytic point of view (Fig. 5, curve 1). OER takes place at 1.5–1.7 V. The average slope \(\frac{dE}{dl}\) makes ~80 mV up to \(i \approx 100\) mA cm\(^{-2}\). OH\(^-\) ions should be involved in this process, since OER becomes significantly hindered as the concentration of OH\(^-\) decreases down to pH 11–12. In slightly alkaline media, the branch of the voltammogram representing OER shifts by ~600 mV towards more positive \(E\) values (Fig. 5, curve 2). This should be related to the passivation of the electrode surface like in the case of the acidic medium (Fig. 4), and also to the change in the mechanism of the oxygen evolution reaction.

Curves 3 and 4 in Fig. 5 represent a more detailed view of the processes taking place on the Ti / RuO\(_2\)-NiO electrode surface in the range of lower current densities. One can see that the transpassivation process begins at \(\approx 1.3\) V. According to literature [19], the anodic current waveform in voltammograms 3 and 4 within \(E\) range from ~1.3 V to ~1.6 V should be related to the oxidation of NiO and Ni(OH\(_2\)) to NiOOH. The branch of voltammograms 3 and 4 beginning at \(E \approx 1.6\) V is related to the catalytic oxidation of O\(^2-\) ions, which could conceivably be represented by the sequence of the following reactions involving the participation of RuO\(_2\) and NiO recently proposed in [18, 20]:

\[
\text{NiOOH} + \text{OH}^- \rightleftharpoons \text{NiO(OH)}_2 + \text{H}^+ + e^- \quad (1)
\]

\[
\text{NiO(OH)}_2 + 2\text{OH}^- \rightarrow \text{NiOO}_2 + 2\text{H}_2\text{O} + 2e^- \quad (2)
\]

\[
\text{NiOO}_2 + \text{OH}^- \rightarrow \text{NiOOOH} + \text{O}_2 + e^- \quad (3)
\]

and

\[
\text{RuO}_2 + \text{OH}^- \rightleftharpoons \text{RuO}_2^+ \cdot (\text{OH}^-)_{ad} + e^- \quad (4)
\]

\[
\text{RuO}_2^+ \cdot (\text{OH}^-)_{ad} + \text{OH}^- \rightarrow \text{RuO}_3 + \text{H}_2\text{O} + e^- \quad (5)
\]

\[
\text{RuO}_3 + 2\text{OH}^- \rightarrow \text{RuO}_4 + \text{O}_2 + \text{H}_2\text{O} + 2e^- \quad (6)
\]

The summary reaction for both cases is:

\[
4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \quad (7)
\]

NiOO\(_2\)_\(_\text{ad}\) in eqs. (2) and (3) represents Ni(IV) peroxide, and RuO\(_2\)_\(_\text{ad}\) is Ru(IV) peroxide or Ru(VI) oxide, which form as intermediates in OER [21]. RuO\(_2^-\) represents a hole in the RuO\(_2\) valence band [20, 22]. When the concentration of OH\(^-\) ions in the solution is sufficiently high, the oxygen evolution process, according to summary reaction (7), begins at \(E \approx 1.5\) V. The above assumption regarding the formation of metal peroxides, which can also be treated as the chemisorption of O\(^2-\) ions on the electrode surface, makes it possible to explain the underpotential occurrence of OER with respect to \(E^{\text{NiO/OH}_2}_{\text{NiO/OH}_2}\) = 1.7 V. In the case of the slightly alkaline solution, the limitation in the rate of the anodic process occurs at \(E \geq 1.7\) V, as can be seen from curves 3 and 4 (Fig. 5). Stirring of the solution has some influence on the rate of the process within 1.7–1.9 V (Fig. 5, curve 4). This influence is too weak, however, to presume that the rate of the process is limited by the diffusion of OH\(^-\) ions. The limitation of the anodic process rate, like in the case of the neutral medium (Fig. 4, curve 4), should be attributed to the formation of a passivating layer of anhydrous NiOOH as a result of further oxidation of NiOOH. At \(E > 2.0\) V, the oxygen evolution reaction on the surface of NiO should proceed irreversibly involving the participation of H\(_2\)O molecules mainly as suggested in [18]:

\[
\text{NiO}_2 + \text{H}_2\text{O} \rightarrow [\text{NiO}_2] + 2\text{H}^+ + 2e^- \quad (8)
\]

\[
[\text{NiO}_2] + \text{H}_2\text{O} \rightarrow \text{NiO}_4 + \text{H}_2\text{O}_2 \quad (9)
\]

\[
\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2e^- \quad (10)
\]

summary equation \(2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-\), (11)

where \([\text{NiO}_2]\) is the unstable intermediate in OER. One can see that in the slightly alkaline solution (Fig. 5, curves 2–4), similarly to the slightly acidic and neutral ones (Fig. 4, curves 3, 4), there is no influence of the RuO\(_2\) component on the rate of the process, since OER on the RuO\(_2\) surface in both acidic and alkaline media begins at \(E \approx 1.4\) V [21]. As can be judged from the cathodic part of cycles 3 and 4 (Fig. 5), the reduction of NiO\(_2\) to NiOOH and NiOOH to NiO mainly takes place within \(E\) range from ~1.8 V to ~1.4 V [19] (Fig. 5, curves 3, 4). The rectangular shape of the voltammograms at \(E < 1.4\) V demonstrates most likely, the presence of RuO\(_2\) on the electrode surface [21].

It is interesting to note that the addition of 0.5 M NaCl to 1 M KOH has almost no effect on the \(E\) evolution process on Ti / RuO\(_2\)-NiO anode, as can be seen from the comparison of curve 1 in Figs. 5 and 6 a. The slope \(\frac{dE}{dl}\) makes ~80 mV up to
Oxygen evolution on composite ruthenium and nickel oxides electrode

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CONCLUSIONS

It has been found that the compound of RuO₂ and NiO oxides thermally deposited on the titanium electrode has a synergetic catalytic effect for the evolution process of O₂ in both strongly acidic and strongly alkaline media.

It has been suggested that Ti / RuO₂ · NiO electrode can be used for obtaining pure oxygen by electrolyzing sea water alkalized to pH ≥ 14.

References

Santrauka