CATALYTIC PROPERTIES AND STABILITY OF NICKEL–TIN POWDER ALLOYS IN THE PROCESS OF ELECTROCHEMICAL HYDROGEN EVOLUTION FROM ALKALI SOLUTION

Abstract. Ni–Sn powder alloys with a nickel content from 24.4 to 78.5 at.% and from 30.6 to 55.1 at.%, respectively, were synthesized chemically and electrochemically for the use as catalysts for the hydrogen electrochemical reduction (HER) in alkali solution. It was established that the catalytically active surface area of chemically synthesized powders was larger in comparison with electrochemically obtained ones. Ni24.4Sn75.6 powder alloy has the largest surface area. It was found that catalytic properties of chemically synthesized powders increased in the row Ni24.4Sn75.6 < Ni78.5Sn21.5 < Ni. Electrochemically obtained alloys are inefficient as HER catalysts. It was found that Ni24.4Sn75.6 alloy is characterized by the greater retention of catalytically active surface area during exploitation in alkali solution in comparison with Ni and Ni78.5Sn21.5 alloy.

Keywords: nickel–tin alloy, electrocatalysis, hydrogen evolution, alkaline solution, corrosion resistance


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**Introduction.** The development of technologies that allow to obtain renewable energy sources is of key importance today due to the global world energy crisis related to the problems with the supply of non-renewable energy sources and their cost rising. An important alternative to non-renewable energy sources is hydrogen energy. There are a number of methods for hydrogen production such as biotechnological (for example, from biomass), steam reforming of methane and natural gas, electrolysis of aqueous solutions, etc. The hydrogen production by electrolysis of strongly acidic or strongly alkaline solutions has a number of advantages compared to other methods: produced hydrogen has high purity; the process of hydrogen production is simple and environmentally-friendly. In the last decade, there are a lot of works related to the elaboration of new electrode materials for the electrochemical hydrogen evolution from aqueous solutions with catalytic activity not inferior then such catalysts as platinum, iridium, rhodium, palladium, and gold used today, but cheaper [1]. The search for effective catalysts is carried out in number ways. For instance, nickel or cobalt alloys with copper, tin, tungsten, etc., composite materials (metal–carbon with different structural organization, metal–semiconductor oxide), metal sulfides and etc. are proposed to be used as electrode materials [2–4].

It is known that hydrogen evolution reaction (HER) in alkali solutions catalyzed with metals proceeds through the following steps: reduction of hydrogen and its adsorption on the catalytically active metal surface (Volmer step (1)); “electrochemical” desorption (Heyrovsky step (2)); “complex” desorption (Tafel step (3)) [2, 4]:

\[
\begin{align*}
M + \text{H}_2\text{O} + e^- & \rightarrow M-\text{H} + \text{OH}^-,
\text{(1)} \\
M-\text{H} + \text{H}_2\text{O} + e^- & \rightarrow \text{H}_2 + M + \text{OH}^-,
\text{(2)} \\
M-\text{H} + M-\text{H} & \rightarrow 2M + \text{H}_2.
\text{(3)}
\end{align*}
\]

One of the ways to increase the catalytic activity of nickel is its alloying with other metals that reduces the hydrogen evolution overpotential by lowering Ni–H bond energy [5–8]. Alloying also improves the stability of catalysts in alkaline solutions, which is important for long-term cyclic operation of electrodes.

Nickel-tin alloys attract special attention of researchers as promising electrode materials (cathodes) for HER in alkaline media. Nickel-tin alloy coatings electrochemically deposited from pyrophosphate-glycinate solutions on nickel meshes or compact nickel substrates [7, 9–12], as well as highly porous materials fabricated by joint pressing of nickel and tin powders were studied as HER catalysts in alkaline media. The catalytic characteristics of porous electrode materials with 65 at.% of nickel are better than those of pure nickel [11]. Electrochemically deposited nickel-tin alloys with 60 at.% of Ni also demonstrate high catalytic activity in HER in 1 mol/dm³ NaOH and 6 mol/dm³ KOH [7, 9, 12].

It was found that the catalytic activity of cathodes with Ni–Sn coatings with 52–73 at.% of Ni gradually decreased during their operation in 8 mol/dm³ NaOH, which was similar to the behavior of commercial Ni–RuO₂ electrode material (De Nora production). However, the alloy was characterized by lower hydrogen evolution overvoltage [9]. It was shown in [10] that electrodeposited Ni–Sn alloy with 73 at.% of Ni exhibited better catalytic activity in HER in alkaline solution than traditionally used nickel mesh or Raney nickel.

It is known that powder alloys obtained by chemical reduction of metal ions have a larger specific surface area than their electrochemically deposited analogs [13]. Therefore, it seems promising to use chemical methods for nickel-tin alloys synthesis to obtain electrode materials for the performance of HER in alkaline solutions.

The purpose of this work was to carry out the comparative study of the catalytic activity of chemically and electrochemically synthesized Ni–Sn powder alloys in HER in alkaline solution, as well as the analysis of catalytic activity retention of the alloys in alkaline solution during cyclic use.

**Experimental part. Synthesis of powder alloys.** Chemical synthesis of Ni–Sn powders was carried out by Ni(II) and Sn(II) ions co-reduction with hydrazine dihydrochloride from the solution (mol/dm³): NiCl₂·6H₂O – 0.02–0.08; SnCl₂·2H₂O – 0.02–0.08; Na₃C₆H₅O₇ – 0.14; NH₃·2HCl – 0.5; NaOH – 3.0. The molar [Sn²⁺] : [Ni²⁺] ratio was equal to 4 : 1 or 1 : 4. Synthesis was carried out at (75 ± 2) °C under continuous stirring until the color of the solution disappeared. Nickel powder was obtained similarly from the solution in the absence of Sn(II) for comparison of catalytic activity.
Electrochemical synthesis of Ni–Sn powders was carried out in galvanostatic mode using a B5-78/6 DC power supply from the solution (mol/dm$^3$): NiCl$_2$·6H$_2$O – 0.1–0.2; SnCl$_2$·2H$_2$O – 0.1–0.2, pH 1.5 (low pH was needed to limit Sn(II) hydrolysis). The molar [Sn$^{2+}$] : [Ni$^{2+}$] ratio was equal to 2 : 1 or 1 : 2, solution temperature was (80 ± 2) °C, current density was 200 A/dm$^2$. Nickel plate (99.9 at.% Ni) was used as the anode, copper foil (99.9 % Cu) was the cathode. The anode area was 10 times larger than the cathode one.

Chemically and electrochemically synthesized powders were separated from the solutions on a glass filter, than washed carefully with distilled water and ethanol, and dried in a desiccator over phosphorus(V) oxide.

**Analysis of powder alloys composition and structure.** The powders morphology was studied by scanning electron microscopy (SEM) using a LEO–1420 microscope (Carl Zeiss, Germany). The metals content in the alloys was determined by energy dispersive X-ray microanalysis (EDX-analysis) using a Rontec Edwin attachment to a LEO–1420 microscope.

The phase composition of the powders was determined with a DRON-3.0 X-ray diffractometer (Bourevestnik, JSC, Russia) using CoK$_\alpha$ radiation ($\lambda = 1.78897$ Å). XRD patterns were recorded at the rate 0.05 deg/min and interpreted using ICDD PDF-2 database.

**Electrochemical investigations.** The electrocatalytic activity of powders was evaluated by cyclic voltammetry (CV) studying the behavior of electrodes with “catalytic ink” containing nickel or Ni–Sn alloy powders in 0.1 mol/dm$^3$ KOH at (20 ± 2) °C and deaeration of solution with argon. The alkali solution was prepared using deionized water (18 MΩ·cm) and analytical grade KOH. The experiments were carried out in a three-electrode cell with a platinum auxiliary electrode and a pseudo-reference electrode. CV curves were recorded using a PGSTAT204 potentiostat-galvanostat (Metrohm Autolab, Netherlands) and Nova 2.1 software. Graphite rod (mark M) was used as a working electrode, on the end surface of which “catalytic ink” was applied. The graphite electrode and “catalytic ink” were prepared for experiments according to the procedure described in our previously published article [14].

The stability of the most promising catalytic materials in alkali solution was evaluated by electrochemical impedance spectroscopy (EIS). The measurements were carried out at potentials of hydrogen evolution starting (reaction (1)) up to the potential –1.4 V, at which hydrogen was actively evolved from 0.1 mol/dm$^3$ KOH and did not create significant noise when recording impedance spectra. The impedance spectra were recorded in the frequency range from 10 kHz to 0.04 Hz, the points number per decade of oscillations was 10, and the oscillations amplitude was 5 mV. The EIS data fitting was performed using Nova 2.1 and EIS Spectrum Analyzer software packages. The data obtained were used for the calculating the capacitance of the electric double layer ($C_{dl}$). It depends on the electrochemically active surface area (ECSA), which is why its retention during cyclic utilization was analysed to judge the stability of catalytic materials [15]. $C_{dl}$ was calculated using the Brug formula [15]. The working electrode was kept at the same potential for 200 s before the EIS measurements to ensure a stable current density.

The “capacitance” method was used to determine ECSA. CV curves were recorded at different potential scan rates ($\nu$) (20, 50, 100, 150, 200, 300, and 400 mV/s) in 0.1 mol/dm$^3$ KOH at potentials ±50 mV around the open circuit potential (non-faradaic processes occur in this potential region). CV curves recording was started after keeping the graphite working electrode with “catalytic ink” in KOH solution for 15 min. The $\Delta I/2 – \nu$ graph was plotted based on the obtained results, where $\Delta I$ is the difference between the values of the anodic ($I_a$) and cathodic ($I_c$) currents (with potential centering). The slope $S$ was determined from this graph, which corresponded to the capacitance of the electric double layer $C_{dl}^*$ (under conditions of non-faradaic processes) according to the formula

$$S = C_{dl}^* [F] = \frac{\Delta I/[A]}{\nu[V/s]},$$

(4)

The ECSA was calculated by the formula

$$ECSA[cm^2] = \frac{C_{dl}^* [\mu F]}{c},$$

(5)

where $c$ was the specific charge density equal to 40 $\mu F/cm^2$ [16].
Results and their discussion. Composition and structure of powder alloys. In the case of chemically synthesized Ni–Sn alloys at molar ratios \([\text{Sn}^{2+}] : [\text{Ni}^{2+}]\) equal to 4 : 1 or 1 : 4, nickel content is 24.4 and 78.5 at.%, respectively (Table 1). The alloys electrochemically deposited at molar ratios \([\text{Sn}^{2+}] : [\text{Ni}^{2+}]\) equal to 2 : 1 or 1 : 2 contain 30.6 and 55.1 at.% of nickel, respectively.

Table 1. Elemental and phase composition of nickel and Ni–Sn alloys powders chemically and electrochemically synthesized and ECSA value calculated from CV results

<table>
<thead>
<tr>
<th>Way of alloy obtaining</th>
<th>([\text{Sn}^{2+}] : [\text{Ni}^{2+}]) ratio in the solution</th>
<th>Elemental composition, at.%</th>
<th>Phase composition</th>
<th>ECSA, cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical reduction (ChR)</td>
<td>1 : 4</td>
<td>21.5 ± 1.9 \text{ Sn}</td>
<td>100.0 \text{ Ni}</td>
<td>\text{Ni, Ni(OH)₂}</td>
</tr>
<tr>
<td></td>
<td>4 : 1</td>
<td>75.6 ± 4.0 \text{ Ni}</td>
<td>24.4 ± 1.2 \text{ Sn}</td>
<td>\text{Ni, β-Sn, Ni₃Sn₂, Ni₅Sn₄, SnO₂}</td>
</tr>
<tr>
<td>Electrochemical reduction (EChR)</td>
<td>1 : 2</td>
<td>44.9 ± 3.2 \text{ Ni}</td>
<td>55.1 ± 5.0 \text{ Sn}</td>
<td>\text{Ni, β-Sn, NiSn, Ni₅Sn₄, Ni₅Sn₆, SnO₂}</td>
</tr>
<tr>
<td></td>
<td>2 : 1</td>
<td>69.4 ± 4.1 \text{ Ni}</td>
<td>30.6 ± 2.8 \text{ Sn}</td>
<td>\text{Ni, β-Sn, NiSn, Ni₃Sn₂, Ni₅Sn₄, SnO₂}</td>
</tr>
</tbody>
</table>

The phase composition of chemically synthesized Ni–Sn powders includes nickel, \(β\)-Sn, \(Ni_3Sn_2\) and \(Ni_5Sn_4\) intermetallics (Table 1). The broadened halos in XRD patterns in the region of diffraction angles 35–75 degrees indicate that the powders are partially crystalline. The crystallinity degree of the powders increases with the growth in the tin content: the halos width decreases, and the reflections intensity increases. Nickel powder consists of crystalline Ni and a small fraction of Ni(OH)₂ (judging by the reflections on the XRD patterns with intensity less than 3% in the range of diffraction angles 35–75 degrees).

Electrochemically synthesized Ni–Sn powders include phases of metals (Ni, \(β\)-Sn) and NiSn, Ni₅Sn₄, Ni₅Sn₆, \(Ni_3Sn_2\) intermetallics (Table 1). It is important to note that a small quantity of SnO₂ is found in Ni–Sn powders obtained by both methods.

The chemically synthesized nickel powder consists of spherical particles with the sizes of 0.2–1.1 \(\mu\)m (the dominating fraction of particles is 0.2 \(\mu\)m) and polygonal shaped plates with a length of 10–70 \(\mu\)m and with small particles adsorbed on their surface (Fig. 1, a).

Ni₇₈.₅Sn₂₁.₅ (ChR) alloy consists of spherical particles with diameter 0.1–0.5 \(\mu\)m, as well as polygonal shaped plates with the length of 1–50 \(\mu\)m, which is similar to nickel powder (Fig. 1, b). Ni₂₄.₄Sn₇₅.₆ (ChR) alloy includes small spherical particles with diameter 0.2–2.0 \(\mu\)m, their average size is larger than for Ni₇₈.₅Sn₂₁.₅ (ChR) alloy (Fig. 1, c). Lamellar polygons similar to nickel and Ni₇₈.₅Sn₂₁.₅ (ChR) Powders are absent in the alloy enriched with tin.

Ni₅₅.₁Sn₄₄.₉ (EChR) alloy consists of small particles forming flower-type aggregates with diameter of 1.7–2.5 \(\mu\)m and dendrites with the length of 2.9–12.2 \(\mu\)m and width of 1.0–2.9 \(\mu\)m (Fig. 1, d). Ni₃₀.₆Sn₆₉.₄ (EChR) powder consists of the dendrites with the length of 2.8–8.1 \(\mu\)m and width of 0.7–2.8 \(\mu\)m (Fig. 1, e), which is explained by the conditions of the alloy synthesis (the current density close to the limiting diffusion) [13].

Electrocatalytic properties of powders. The highest ECSA value (2.06 cm²) corresponds to Ni₂₄.₄Sn₇₅.₆ (ChR) alloy while Ni₇₈.₅Sn₂₁.₅ (ChR) Powder is characterized by 1.6 times lower value (Table 1). It is worth noting that the nickel powder synthesized in chemical way has a lower ECSA value in comparison with the chemically synthesized Ni–Sn alloys. The minimum ECSA value (0.38 cm²) corresponds to the electrochemically synthesized Ni₅₅.₁Sn₄₄.₉ (EChR) alloy.

The powders catalytic activity in HER in 0.1 mol/dm³ KOH was evaluated only after the electrode with “catalytic ink” had been worked through for five cycles of the potential scan since the potential of hydrogen evolution starting practically ceased to change (changes did not exceed 1.0–1.5%) (Fig. 2). Moreover, starting from the fifth cycle, the current density (\(j\)) ceased to change with further cycling at the potential –1.45 V (the potential at which the Heyrovsky and Tafel steps are realized [2, 4]).

The criteria for evaluating the catalytic activity of the powders was the value of the potential of the working electrode at \(j = 10 \text{ mA/cm}²\) (\(j_{\text{lim}}\)) (the value when the conversion efficiency of solar energy into hydrogen is estimated, equal to 12.3 % [2, 17]). In the case of Ni powder catalysis, HER starts at the
potential –0.87 V; the potential value corresponding to $j_{10}$ equal to –1.26 V (Fig. 3, a). In the case of Ni78.5Sn21.5$_{(ChR)}$ and Ni24.4Sn75.6$_{(ChR)}$ alloys, HER starts at more negative potentials than for Ni (–1.01 V and –1.18 V, respectively); $j_{10}$ value is reached at more negative potentials (–1.38 V and –1.40 V, respectively) (Fig. 3, b and c).

Small peaks with current densities from 1.2 to 2.2 mA/cm$^2$ in the potential range of −(0.60–0.99) V are observed in the anodic scans of CV curves for Ni78.5Sn21.5$_{(ChR)}$ and Ni24.4Sn75.6$_{(ChR)}$ powders (Fig. 3, b and c). The authors of [9, 18, 19] attribute these peaks to the several processes occurring simultaneously: oxidation of adsorbed hydrogen and nickel with the formation of α-Ni(OH)$_2$. Tin is oxidized at the potential −0.75 V (Fig. 3, c) (this has been revealed when recording CV curve for working electrode with “catalytic ink” containing tin powder).

The comparison of the characteristics of cathodic scans in CV curves in alkaline solution for chemically synthesized powders of nickel and its alloys with tin demonstrates that Ni powder has the best catalytic ability.
CV curves for working electrodes with electrochemically synthesized Ni–Sn alloys included into “catalytic ink” are presented in Fig. 4. The current associated with HER on Ni$_{55.1}$Sn$_{44.9}$ (EChR) and Ni$_{30.6}$Sn$_{69.4}$ (EChR) powders is observed in the cathodic scans at the potentials –1.25 and –1.46 V, respectively. The current density $j_{10}$ is not reached at potential sweep up to –1.5 V, which indicates the inefficiency of application of such alloys in HER catalysis.

Fig. 2. The dependence of $j$ value at $E = –1.45$ V on the number of scan cycles of a graphite electrode with “catalytic ink” containing powders of nickel or chemically synthesized Ni–Sn alloys.

Fig. 3. CV curves (tenth cycle) recorded in 0.1 mol/dm$^3$ KOH on a graphite electrode with “catalytic ink” containing powders: $a$ – Ni; $b$ – Ni$_{78.5}$Sn$_{21.5}$ (ChR); $c$ – Ni$_{24.4}$Sn$_{75.6}$ (ChR).

CV curves for working electrodes with electrochemically synthesized Ni–Sn alloys included into “catalytic ink” are presented in Fig. 4. The current associated with HER on Ni$_{55.1}$Sn$_{44.9}$ (EChR) and Ni$_{30.6}$Sn$_{69.4}$ (EChR) powders is observed in the cathodic scans at the potentials –1.25 and –1.46 V, respectively. The current density $j_{10}$ is not reached at potential sweep up to –1.5 V, which indicates the inefficiency of application of such alloys in HER catalysis.
Comparison of the catalytic properties in HER reactions of Ni–Sn alloys (with tin content of 20–80 at.%) synthesized in this work and in the works [7, 9–12] with different structural organization – porous powders obtained by chemical reduction of Sn(II) and Ni(II) or by pressing metallurgical Ni and Sn powders, Ni–Sn alloy coating electrochemically deposited onto a nickel grid with different cell parameters, causes difficulties. The reasons for the difficulties are related to the fact that the authors of these works carried out the electrochemical experiments in KOH solutions with different concentrations 0.1–6.0 mol/dm$^3$, at different potential sweep rates, and did not evaluate the stability of catalytic activity electrode during long-term operation. However, it should be noted that the catalytic properties of the Ni$^{78.5}$Sn$^{21.5}$ alloy are similar to those for a porous alloy containing 15 at.% tin formed from metallurgical Ni and Sn powders, which is characterized as the best in [7], despite the fact that the experiment in this work was carried out in 6 mol/dm$^3$ solution of KOH.

Analysis of catalytic activity retention of alloys. Since chemically synthesized powders exhibited better catalytic activity compared to electrochemically obtained powders, the evaluation of stability in 0.1 mol/dm$^3$ KOH (changes in $C_{dl}$) by EIS method was carried out only for Ni and Ni$^{78.5}$Sn$^{21.5}_{(ChR)}$, Ni$^{30.6}$Sn$^{75.4}_{(ChR)}$ alloys. The impedance spectra (Nyquist and Bode plots) recorded on a graphite electrode with “catalytic ink” with nickel powder at the potential –1.20 V are presented in Fig. 5, a and b. The spectra for other potentials and electrodes with “catalytic ink” containing chemically deposited Ni–Sn alloys are similar, only their parameter changes.

Squashed semicircle is observed in all obtained Bode plots. Such semicircle corresponds to the spectra for porous electrodes [20]. Charge transfer resistance of a non-ideal capacitor and the porous film resistance ($R_{por}$) are represented in the equivalent circuit by a constant phase element (CPE). The equivalent circuit selected for the spectra is shown in Fig. 5, c. According to the literature data [20–22], the semicircle in the high-frequency region weakly depends on the potential and is related to the electrode porosity, while the semicircle in the low-frequency region is due to the faradaic process at the cathode (hydrogen evolution in this case).

The parameters of equivalent circuits determined from impedance spectra recorded at different potentials of a graphite electrode with “catalytic ink” containing Ni or Ni–Sn powders are presented in Table 2. The values of the average double layer capacitance $C_{dl}$ were calculated from the data obtained.

The comparison of the change in the parameter $\alpha_{dl}$, which characterizes the surface “non-ideality”, after the first and tenth scan cycles of the working electrodes with “catalytic ink” containing different metal powders at the potential of active HER shows that it decreases for Ni, Ni$^{78.5}$Sn$^{21.5}_{(ChR)}$ and Ni$^{24.4}$Sn$^{75.6}_{(ChR)}$ powders by the values of 15, 2 and 12 %, respectively. The decrease in the values of $C_{dl}$ and $\alpha_{dl}$ with the growth in the number of operation cycles indicates the decrease in ECSA. However, the highest values of $C_{dl}$ and $\alpha_{dl}$ before and after tenfold cycling characterize the Ni$^{24.4}$Sn$^{75.6}_{(ChR)}$ powder, i.e. this alloy is more stable during operation in comparison with the chemically synthesized powders of Ni or Ni$^{24.4}$Sn$^{75.6}_{(ChR)}$ alloy.
Table 2. Parameters obtained by fitting EIS results recorded at different potentials in 0.1 mol/dm³ KOH for electrodes with “catalytic ink” containing chemically synthesized Ni or Ni–Sn powders

<table>
<thead>
<tr>
<th>Powder</th>
<th>$E$, V</th>
<th>$R_s$, $\Omega$</th>
<th>$\alpha_{por}$</th>
<th>$R_{por}$, k$\Omega$</th>
<th>$\alpha_{dl}$</th>
<th>$R_{dl}$, k$\Omega$</th>
<th>$CPE_{por}$, $\mu$F/cm²</th>
<th>$CPE_{dl}$, $\mu$F/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>–1.00</td>
<td>142.0</td>
<td>0.46</td>
<td>3.7</td>
<td>0.82</td>
<td>20.8</td>
<td>333</td>
<td></td>
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<tr>
<td></td>
<td>–1.10</td>
<td>121.4</td>
<td>0.43</td>
<td>12.6</td>
<td>0.59</td>
<td>7.9</td>
<td>151</td>
<td></td>
</tr>
<tr>
<td></td>
<td>–1.20</td>
<td>113.7</td>
<td>0.24</td>
<td>10.9</td>
<td>0.54</td>
<td>3.5</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>–1.30</td>
<td>144.5</td>
<td>0.37</td>
<td>0.05</td>
<td>0.52</td>
<td>1.5</td>
<td>19</td>
<td></td>
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<tr>
<td></td>
<td>–1.40</td>
<td>171.4</td>
<td>0.32</td>
<td>0.14</td>
<td>0.60</td>
<td>0.50</td>
<td>51</td>
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<td></td>
<td>(1th cycle)</td>
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<td></td>
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<tr>
<td></td>
<td>–1.40</td>
<td>122.0</td>
<td>0.30</td>
<td>0.07</td>
<td>0.51</td>
<td>0.52</td>
<td>31</td>
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<tr>
<td>Ni78.5 Sn21.5 (ChR)</td>
<td>–1.21</td>
<td>229.8</td>
<td>0.34</td>
<td>19.8</td>
<td>0.72</td>
<td>9.1</td>
<td>107</td>
<td></td>
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<tr>
<td></td>
<td>–1.26</td>
<td>209.6</td>
<td>0.28</td>
<td>0.3</td>
<td>0.56</td>
<td>7.3</td>
<td>22</td>
<td></td>
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<tr>
<td></td>
<td>–1.31</td>
<td>223.9</td>
<td>0.26</td>
<td>1.0</td>
<td>0.54</td>
<td>3.9</td>
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<tr>
<td></td>
<td>–1.36</td>
<td>273.9</td>
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<td>0.3</td>
<td>0.53</td>
<td>2.2</td>
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<td></td>
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<td></td>
<td>(1th cycle)</td>
<td></td>
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<tr>
<td></td>
<td>–1.40</td>
<td>246.3</td>
<td>0.35</td>
<td>0.1</td>
<td>0.49</td>
<td>1.3</td>
<td>10</td>
<td></td>
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<td></td>
<td>(10th cycle)</td>
<td></td>
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<td></td>
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<tr>
<td>Ni24.4 Sn75.6 (ChR)</td>
<td>–1.15</td>
<td>83.8</td>
<td>0.45</td>
<td>7.2</td>
<td>0.90</td>
<td>11.0</td>
<td>1140</td>
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<tr>
<td></td>
<td>–1.21</td>
<td>88.8</td>
<td>0.47</td>
<td>9.0</td>
<td>0.84</td>
<td>4.2</td>
<td>830</td>
<td></td>
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<tr>
<td></td>
<td>–1.28</td>
<td>85.3</td>
<td>0.48</td>
<td>1.6</td>
<td>0.79</td>
<td>1.4</td>
<td>599</td>
<td></td>
</tr>
<tr>
<td></td>
<td>–1.34</td>
<td>102.9</td>
<td>0.46</td>
<td>1.4</td>
<td>0.78</td>
<td>0.5</td>
<td>858</td>
<td></td>
</tr>
<tr>
<td></td>
<td>–1.40</td>
<td>144.6</td>
<td>0.30</td>
<td>0.3</td>
<td>0.66</td>
<td>0.2</td>
<td>139</td>
<td></td>
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<tr>
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<td>(1th cycle)</td>
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<td></td>
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<tr>
<td></td>
<td>–1.40</td>
<td>169.5</td>
<td>0.24</td>
<td>0.2</td>
<td>0.58</td>
<td>0.5</td>
<td>106</td>
<td></td>
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<tr>
<td></td>
<td>(10th cycle)</td>
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* The parameters $\alpha_{por}$ and $\alpha_{dl}$ characterize porosity and the surface “non-idealitity”, respectively.
Conclusion. Ni–Sn powder alloys with a nickel content 24.4 and 78.5 at.%, including Ni, β-Sn, Ni$_3$Sn$_2$, Ni$_4$Sn$_3$, SnO$_2$ crystalline phases, were obtained by chemical reduction with hydrazine dihydrochloride as a reducing agent. Nickel-tin alloys with a nickel content 30.6 and 55.1 at.%, consisting of Ni, β-Sn, NiSn, Ni$_3$Sn, Ni$_3$Sn$_2$, Ni$_4$Sn$_3$ crystalline phases, were electrochemically synthesized from an acidic chloride solution.

It was established that the electrochemically active surface area of chemically synthesized powders was greater than that of electrochemically obtained ones. Chemically deposited Ni$_2$4.4Sn75.6 alloy has the maximum electrochemically active surface area, this alloy consists of small, practically non-aggregated particles with 0.2–2.0 μm in sizes. The electrochemically synthesized Ni–Sn alloys are represented by dendritic structures and characterized by minimum surface area that limits their catalytic activity.

It was found that catalytic activity of chemically synthesized powders increases in the row Ni$_2$4.4Sn75.6 < Ni78.5Sn21.5 < Ni; electrochemically synthesized powder alloys were inefficient in HER catalysis. It was found that the chemically deposited Ni$_2$4.4Sn75.6 alloy characterized by a greater retention of the catalytically active surface area during cyclic operation in comparison with nickel or Ni78.5Sn21.5 alloy.

Acknowledgements. This work was financially supported by the Belarusian republican foundation for fundamental research (grants no. X20MH-004, X23MH-002).

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