



*J. Serb. Chem. Soc.* 84 (11) 1271–1286 (2019)  
JSCS–5263

## Corrected accelerated service life test of electrodeposited NiSn alloys and Ni as cathodes for industrial alkaline water electrolysis

VLADIMIR D. JOVIĆ<sup>1\*</sup>, BORKA M. JOVIĆ<sup>1#</sup>, NEVENKA R. ELEZOVIĆ<sup>1#</sup>  
and LJILJANA GAJIĆ-KRSTAJIĆ<sup>2#</sup>

<sup>1</sup>Institute for Multidisciplinary Research University of Belgrade, P. O. Box 33, 11030 Belgrade, Serbia and <sup>2</sup>Institute of Technical Sciences Serbian Academy of Science and Arts, Knez Mihajlova 35, 11000 Belgrade, Serbia

(Received 15 May, revised 3 July, accepted 5 July 2019)

**Abstract:** The “corrected accelerated service life test for hydrogen evolution reaction” (CASLT-HER), designed for application of certain electrode materials as cathodes in the cell for alkaline water electrolysis in 30 % KOH at 80 °C, was performed at electrodeposited NiSn alloy and Ni 40 mesh electrodes. The Ni 40 mesh was slightly etched, while the NiSn alloy coating was electrodeposited from the bath containing pyrophosphate, glycine, SnCl<sub>2</sub> and NiCl<sub>2</sub> onto Ni 40 mesh to the thickness of approximately 40 μm. It is shown that the NiSn cathode possess from maximum 0.77 V to minimum 0.30 V better overpotential than the Ni 40 mesh electrode during the 5 years of their exploitation at the conditions of industrial alkaline water electrolysis. It is also shown that both electrodes should be held at  $j = -0.3 \text{ A cm}^{-2}$  for at least 5 h in order to establish stable overpotential response. The limiting overpotential values for applying cyclic voltammetry (CVs, to mimic “polarity inversion”) should be determined in a separate experiment before the CASLT-HER and should be adjusted during the application of CVs.

**Keywords:** constant current density; cyclic voltammetry; hydrogen evolution.

### INTRODUCTION

In our recent paper<sup>1</sup> the electrodeposited NiSn coating was compared with Ni 40 mesh and Ni coating electrodeposited from the Watts type bath onto Ni 40 mesh, using “accelerated service life test” (ALST), for the HER and the OER under the conditions of industrial alkaline water electrolysis. ALST was based on the service life test designed for testing cathode materials under the conditions of industrial electrolysis in chlor-alkali cells.<sup>2–5</sup>

\* Corresponding author. E-mail: vladajovic@imsi.bg.ac.rs

# Serbian Chemical Society member.

<https://doi.org/10.2298/JSC190515074J>

To use certain electrode materials as cathodes in the industrial process of alkaline water electrolysis, the most important factors that should be considered are: overpotentials for the HER at a high current density (usually  $-0.3 \text{ A cm}^{-2}$ ), as well as high stability of the electrodes in industrial cells. As it was already shown for the chlor-alkali electrolysis,<sup>2-5</sup> the loss of catalytic activity and stability of cathodes during their exploitation in industrial cells is the result of the “polarity inversion” of the electrodes, which takes place during the replacement of old electrodes of a certain number of electrolyzers with the new ones in the zero-gap cells. During this operation in one set of the cells, the anodes and cathodes in the rest of the cells are short-circuited, causing a reverse current flow which may damage the cathodes and negatively affect their activity for the HER, while anodes are practically insensitive to the polarity change. The producers of chlorine in chlor-alkali process predicted how often in a certain period of time such operation should be performed and, in accordance with that, designed appropriate ASLT for cathodes.<sup>2-5</sup> The procedure of the ASLT is based on a sequence of galvanostatic polarizations in the HER range and CVs in a wide potential range between the potential of the HER and the potential of the OER (simulating the conditions of “polarity inversion”<sup>2</sup>). Such ASLT could also be applied at the cathodes and anodes for the industrial alkaline water electrolysis, as it was shown in our recent work.<sup>1</sup> Of course, only manufacturer knows acceptable limits of the potential change of electrodes during such test. In our recent work,<sup>1</sup> it was assumed that during the application of either cathodic (HER), or anodic (OER) current density, the duration of a constant current density should be defined by the stable potential response with the time. So, for the HER at Ni electrodes it was necessary to apply  $j = -0.3 \text{ A cm}^{-2}$  for at least 2000 s, while stable potential response for NiSn coating was registered practically immediately after application of cathodic current density (its value was taken after 1000 s). In the case of OER duration of anodic current density was 1000 s. It should be emphasized that such tests were performed after recording polarization curves for both reactions on all three electrodes and that polarization curves were recorded after HER or OER for 10 min. at  $|j| = 0.3 \text{ A cm}^{-2}$ . The question arises, was the time of cathodic and anodic polarization at  $|j| = 0.3 \text{ A cm}^{-2}$ , particularly for Ni electrodes,<sup>9</sup> long enough for correct value of overpotential responses? At the same time the overpotential limits for the CVs were the same for all electrodes, while in some cases the beginning of the OER could not be detected on the CVs (Figs. 5 and 7 of Ref.<sup>1</sup>).

It was shown earlier that electrodeposited NiSn alloys possess high catalytic activity for the HER in alkaline solutions<sup>6,7</sup> and this behavior was tested in our previous works.<sup>8,9</sup> The catalytic activity for the HER in alkaline solutions was mainly the consequence of the presence of high amount (about 80 %) of the hexagonal  $\text{Ni}_{(1+x)}\text{Sn}$  ( $0 < x < 0.5$ ) phase, which was dominant in samples electro-

deposited at the cathodic current densities higher than  $-20 \text{ mA cm}^{-2}$ , as well as of the high roughness of such NiSn coatings.<sup>8</sup>

As it is shown earlier,<sup>10–13</sup> during the HER at Ni electrodes the formation of  $\alpha$ -NiH and  $\beta$ -NiH phases occurred. It was shown that the overpotential for the HER at the Ni electrode increases significantly with the time in 30 % KOH at 80 °C at the cathodic current densities higher than  $-0.1 \text{ A cm}^{-2}$ ,<sup>10</sup> due to the hydride (111) NiH and (200) NiH formation at active Ni cathode surfaces. Taking into account that the behavior of NiSn electrodes during a long time of the HER (at least 5 h) has not yet been investigated, in this work both electrodes were exposed to the extended HER and the corrected accelerated service life test for hydrogen evolution reaction (CASLT-HER) was applied after such treatment. In accordance with the above-mentioned statements, before applying the CASLT-HER, it was necessary to define exact time duration for each electrode to establish stable overpotential response for the HER. At the same time, it was necessary to determine appropriate potential limits used for the CVs. These limits are different for each electrode and before applying the CASLT-HER, certain experiments must be performed to define cathodic and anodic potential limits during the CV experiments. Hence, a new test, CASLT-HER, has been designed in this work, based on the results of extended HER and determination of the proper values of the cathodic and anodic potential limits for the CVs. Such tests were applied to both, NiSn and Ni 40 mesh electrodes, and obtained results are presented.

#### EXPERIMENTAL

All solutions were made from *p.a.* chemicals (Aldrich–Sigma) in extra pure (18.2 M $\Omega$  cm) UV water (Smart2, PureUV, TKA), while all experiments were performed by using potentiostat Reference 600 (Gamry Instruments Inc.).

##### *NiSn samples*

The electrodeposition of NiSn coatings onto the Ni 40 mesh substrate (dimensions 1 cm $\times$ 1 cm; geometric surface area 1.57 cm<sup>2</sup>) was performed in a cell with two Pt counter electrodes (dimensions 2 cm $\times$ 2 cm) placed parallel to the working electrode in the solution containing 0.6 mol dm<sup>-3</sup> K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> + 0.1 mol dm<sup>-3</sup> NiCl<sub>2</sub>·6H<sub>2</sub>O + 0.03 mol dm<sup>-3</sup> SnCl<sub>2</sub>·2H<sub>2</sub>O + 0.3 mol dm<sup>-3</sup> NH<sub>2</sub>CH<sub>2</sub>COOH (pH 6.7) at 25 °C. The NiSn sample was electrodeposited by applying a constant current density of  $-0.1 \text{ A cm}^{-2}$  for 1000 s. Before the electrodeposition of NiSn coatings the Ni 40 mesh substrates were only shortly etched in 1:3 mixture of H<sub>2</sub>O:HNO<sub>3</sub> and washed with the distilled water.

##### *Ni 40 mesh sample*

The Ni 40 mesh samples were only shortly etched in 1:3 mixture of H<sub>2</sub>O:HNO<sub>3</sub> and washed with the distilled water before the experiments.

##### *Recording of the overpotential change with the time for the HER*

The overpotential change with the time ( $\eta$ - $t$ ) at  $j = -0.3 \text{ A cm}^{-2}$  for the HER at both investigated samples was tested in 30 % KOH solution in extra pure UV water at the temperature of 80 °C (industrial electrolyte concentration). For freshly prepared electrodes tests were lasting until a stable overpotential response for the time of at least 5 h has been estab-

lished with following criterion being adopted: if the overpotential change during 2 h of the electrolysis was lower than 10 mV an average overpotential value was used as a stable overpotential response ( $\eta_s$ ). During the CASLT-HER the same criterion was adopted.

Three-compartment cell, specially designed for such samples was used: working electrode of the surface area of 1.57 cm<sup>2</sup> was placed in a central compartment together with the Luggin capillary; two Pt mesh counter electrodes of larger surface areas were placed in the separate compartments each (parallel to the working electrode mesh), so that the oxygen evolved at the counter electrode could not enter the working electrode compartment. Reversible hydrogen electrode (RHE) as a reference electrode was placed in a side compartment connected to the central one through a bridge and a Luggin capillary and was kept at the room temperature.

#### *The overpotential limits for the CV experiments*

The overpotential limits for the CV experiments,  $\eta_{\text{lim-H}}$  and  $\eta_{\text{lim-O}}$ , were determined in separate experiments, using the same electrolyte at the same temperature for freshly prepared electrodes. In order to simulate industrial conditions, it was necessary to reach potentials of the HER and the OER, *i.e.*, to apply overpotentials at which the beginning of these reactions could be detected on the CVs. The value of  $\eta_{\text{lim-H}}$  was determined by recording  $\eta-t$  dependence at  $j = -0.015$  A cm<sup>-2</sup>, while  $\eta_{\text{lim-O}}$  determination was explained in Experimental section

#### *Recording the CVs*

After recording of the overpotential change with the time for the HER and the overpotential limits, five CVs were recorded starting at  $\eta_{\text{lim-H}}$  and finishing at  $\eta_{\text{lim-O}}$ . During the cycling procedure the values of  $\eta_{\text{lim-H}}$  and  $\eta_{\text{lim-O}}$  were always adjusted to provide predicted current densities (as much as possible) for both, HER and OER. It should be emphasized here that for the OER current density limit during the CVs would always be higher than 0.015 A cm<sup>-2</sup>, due to the process Ni(OH)<sub>2</sub>→NiOOH, which is taking place just before the OER. In such a case the  $\eta_{\text{lim-O}}$  were adjusted according to the procedure schematically presented with arrows in Fig. 2. In some cases, it was necessary to adjust the values of  $\eta_{\text{lim-H}}$  too, as shown in Fig. 2.

#### *CASLT-HER procedure*

The CASLT-HER experiments for both cathodes were performed in a following sequence of steps: step (1) – electrode was kept at  $j = -0.3$  A cm<sup>-2</sup> for the time necessary to establish constant overpotential response (5 h) and corresponding  $\eta-t$  response was recorded; step (2) – electrode was kept at a constant overpotential ( $\eta_{\text{lim-H}}$ ) at which  $j_{\text{lim-H}} = -0.015$  A cm<sup>-2</sup> for 200 s; step (3) – electrode was cycled (5 cycles) in the overpotential range from  $\eta_{\text{lim-H}}$  to  $\eta_{\text{lim-O}}$ , with a sweep rate of 50 mV s<sup>-1</sup> and corresponding CVs were recorded. This procedure (steps (1) to (3)) was repeated 5 times, until the number of CVs reached 25. After the 25<sup>th</sup> cycle electrode was kept again at  $j = -0.3$  A cm<sup>-2</sup> for the time necessary to establish constant overpotential response and corresponding (last)  $\eta-t$  response was recorded. The overpotential responses measured at  $j = -0.3$  A cm<sup>-2</sup> were not corrected for the IR drop since the ohmic resistance (obtained from the EIS measurement) was very low, maximum 0.03  $\Omega$  cm<sup>2</sup>, producing maximum change in the overpotential of about 9 mV at  $j = -0.3$  A cm<sup>-2</sup>.

#### *Characterization of samples*

The appearance of electrode surfaces were investigated with a scanning electron microscope (SEM) Tescan VEGA TS 5130 MM.

## RESULTS AND DISCUSSION

*Electrodeposition of the NiSn coatings*

For both electrodes several samples had to be prepared in order to perform all necessary tests explained in Experimental section, since each test was repeated three times. As in our recent work,<sup>1</sup> 0.03 M SnCl<sub>2</sub> was used for the NiSn coatings electrodeposition (see Experimental) and the NiSn samples were electrodeposited by the controlled potential coulometry at  $-1.3$  V vs. SCE to the charge of  $100$  C cm<sup>-2</sup>, while for the CASLT-HER NiSn coatings were electrodeposited at a constant current density  $j_d = -0.1$  A cm<sup>-2</sup> to the charge of  $100$  C cm<sup>-2</sup>.

*Determination of  $\eta_{s,HER}$  and  $\eta_{lim-H}$  during the HER for freshly prepared electrodes*

Following procedures explained in Experimental section the values of  $\eta_{s,HER}$  and  $\eta_{lim-H}$  during the HER onto NiSn coating and Ni 40 mesh electrodes were determined and presented in Fig. 1. The NiSn sample showed relatively stable overpotential response for 5 h, changing from about  $-0.136$  to about  $-0.170$  V. During the first 3 h this change was more pronounced, while from 3 to 5 h of the HER practically constant overpotential response,  $\eta_{s,HER} = -0.169$  V, was recorded. When, after 5 h at  $j = -0.3$  A cm<sup>-2</sup>, the  $j = -0.015$  A cm<sup>-2</sup> was applied, stable overpotential response  $\eta_{lim-H} = -0.042$  V was detected (inset of Fig. 1a). Hence,  $\eta_s = -0.169$  V, recorded during the step (1) in the procedure explained in Experimental could be considered as the overpotential value of the NiSn electrode during the HER before the first “polarity inversion”.

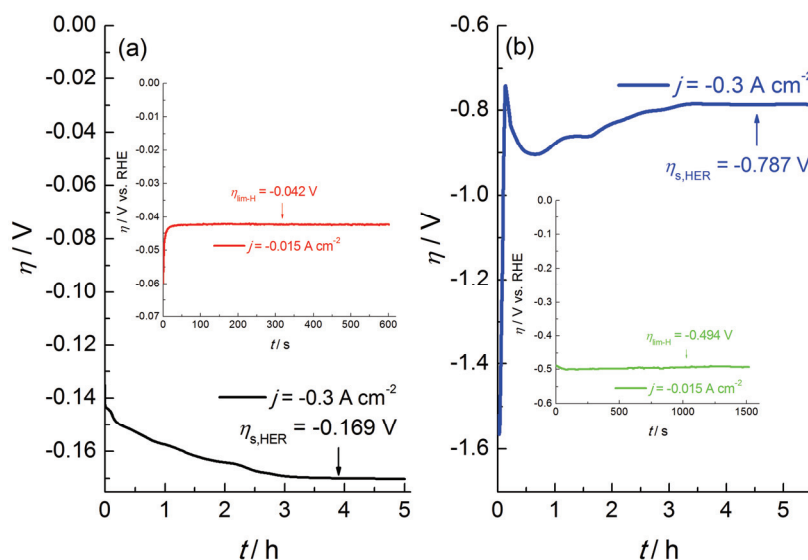


Fig. 1. Overpotential response of the samples NiSn (a) and Ni 40 mesh (b) during long time HER at  $j = -0.3$  A cm<sup>-2</sup>. Insets: overpotential responses ( $\eta_{lim-H}$ ) after applying  $j = -0.015$  A cm<sup>-2</sup>.

The Ni 40 mesh sample showed sharp decrease of the overpotential response during the first 100 s, and, after reaching about  $-0.74$  V, sharp increase in overpotential value from about  $-0.74$  to about  $-0.90$  V. After about 0.7 h the overpotential started to increase slowly to the value  $\eta_{s,HER} = -0.787$  V, which was established after 3.5 h of the HER (Fig. 1b). At the current density  $j = -0.015$  A cm<sup>-2</sup> stable overpotential response  $\eta_{lim-H} = -0.494$  V was established after 50 s (inset of Fig. 1b).

#### Recording the first five CVs after the HER

Results of the next step, recording the first five CVs, are presented in Fig. 2 for both samples. For these experiments preliminary value of  $\eta_{lim-O}$  was obtained by applying  $j = 0.015$  A cm<sup>-2</sup> and recording  $\eta-t$  dependence at both samples. The value recorded after 1000 s was used as  $\eta_{lim-O}$ .

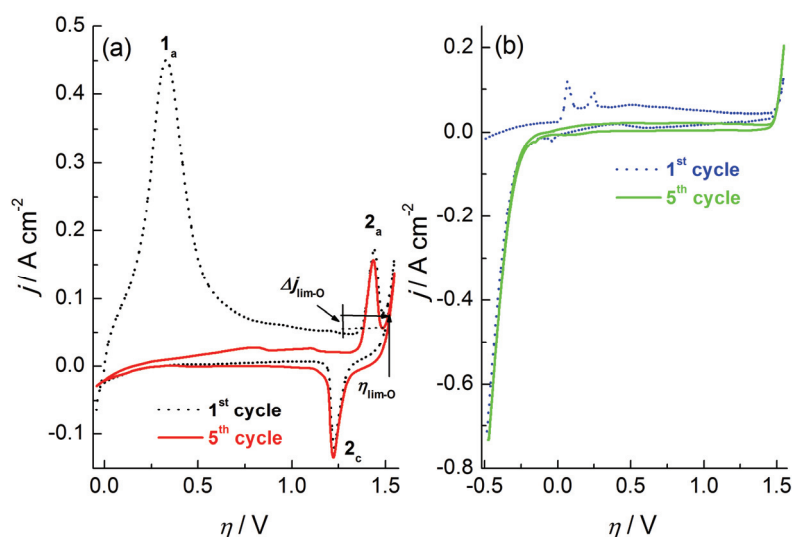


Fig. 2. 1<sup>st</sup> and 5<sup>th</sup> CV recorded at NiSn (a) and Ni 40 mesh (b) electrodes at  $v = 50$  mV s<sup>-1</sup> after HER at  $j = -0.3$  A cm<sup>-2</sup> for 5 h and after holding electrodes at  $\eta_{lim-H}$  for 200 s.

#### NiSn coating sample

The 1<sup>st</sup> and 5<sup>th</sup> cycle (cycles 2–5 were practically identical), recorded at the sweep rate of 50 mV s<sup>-1</sup>, after long time hydrogen evolution (5 h) and after holding NiSn electrode at  $\eta_{lim-H} = -0.494$  V for 200 s, are presented in Fig. 2a. As in our recent work,<sup>1</sup> the first CV is characterized with a large anodic peak positioned at about  $\eta = 0.3$  V (peak 1<sub>a</sub>) and a pair of peaks 2<sub>a</sub> and 2<sub>c</sub> corresponding to the Ni(OH)<sub>2</sub> ↔ NiOOH reaction.<sup>14–16</sup> Already at the second cycle peak 1<sub>a</sub> disappears, while the pair of 2<sub>a</sub> and 2<sub>c</sub> peaks remains on the CVs. As it was already stated in our previous work “huge anodic peak in the 1<sup>st</sup> cycle cor-

responds mainly to the oxidation of adsorbed and absorbed hydrogen entrapped in the pores, partially to the  $\text{Ni}(\text{OH})_2$  formation<sup>14–16</sup> and partially to the  $\text{Ni}_{(1+x)}\text{Sn}$  metastable phase oxidation". Considering Fig. 2a, it appears that the preliminary value of  $\eta_{\text{lim-O}}$  is too large and the  $j_{\text{lim-O}}$  is much higher (reaching  $0.15 \text{ A cm}^{-2}$ ) at  $\eta_{\text{lim-O}} = 1.55 \text{ V}$ . In order to define new value for  $\eta_{\text{lim-O}}$ , a value of  $\Delta j_{\text{lim-O}} = 0.015 \text{ A cm}^{-2}$  (marked with the arrow) was added to the minimum current density after peak 2<sub>a</sub> (dotted line) and the value  $\eta_{\text{lim-O}} = 1.52 \text{ V}$  (also marked with the arrow) was obtained and used in the CASLT-HER.

#### *Ni 40 mesh sample*

Before recording CVs presented in Fig. 2b Ni 40 mesh was held at  $\eta_{\text{lim-H}} = -0.494 \text{ V}$  for 200 s and the current density was about  $-0.013 \text{ A cm}^{-2}$ . The 1<sup>st</sup> and 5<sup>th</sup> CV (2<sup>nd</sup> and 5<sup>th</sup> cycle are practically the same) are seen to be very different. It is important to note high values of current densities recorded for 2<sup>nd</sup>–5<sup>th</sup> cycles at the  $\eta_{\text{lim-H}} = -0.494 \text{ V}$  ( $j = -0.75 \text{ A cm}^{-2}$ ) and at the  $\eta_{\text{lim-O}} = 1.55 \text{ V}$  ( $j = 0.2 \text{ A cm}^{-2}$ ). It is obvious that both limits,  $\eta_{\text{lim-H}}$  and  $\eta_{\text{lim-O}}$ , should be corrected according to the CVs shown in Fig. 3. In Fig. 3a are presented CVs recorded after the HER in the solution saturated with  $\text{H}_2$ . In Fig. 3b are shown CVs recorded in the potential range between  $\eta_{\text{lim-H}}$  and  $\eta_{\text{lim-O}}$  determined at the CVs presented in Fig. 3a. As can be seen in Fig. 3a, during the 1<sup>st</sup> cycle two sharp peaks (1<sub>a</sub> and 2<sub>a</sub>), most probably corresponding to the dissolution of the  $\alpha$ -NiH and  $\beta$ -NiH phases,<sup>10–13</sup> were detected on the CV, with a broad peak 3<sub>a</sub> most probably corresponding to the formation of  $\text{Ni}(\text{OH})_2$ . The peaks 4<sub>a</sub> and 4<sub>c</sub>, corresponding to the  $\text{Ni}(\text{OH})_2 \leftrightarrow \text{NiOOH}$  reaction<sup>14–16</sup> could hardly be detected. The next 4 cycles were practically the same, showing disappearance of all anodic peaks. The presence of shoulder 3<sub>a</sub> and broad peak 1<sub>c</sub>, 2<sub>c</sub>, together with a large current density in the "double layer region", between 0.0 and 1.5 V, indicate that some oxidation and reduction processes are taking place on the electrode surface. At the same time this electrode showed extremely high activity towards the HER. After applying corrected values for  $\eta_{\text{lim-H}}$  and  $\eta_{\text{lim-O}}$  the CVs presented in Fig. 3b are seen to have a "normal" shape, being characterized with a peak of  $\text{Ni}(\text{OH})_2$  formation (1<sub>a</sub>) and a pair of peaks of the  $\text{Ni}(\text{OH})_2 \leftrightarrow \text{NiOOH}$  reaction<sup>14–16</sup> (4<sub>a</sub>, 4<sub>c</sub>). With the increase of cycle numbers additional peak, 5<sub>c</sub>, appeared on the CV, indicating eventual formation of additional phase in the region of the OER.<sup>9</sup> Considering presented results in Fig. 3a it appears that after dissolution of the  $\alpha$ -NiH and  $\beta$ -NiH phases formed during a long time hydrogen evolution, Ni 40 mesh became significantly more active towards the HER, indicating that the "polarity inversion" of Ni 40 mesh cathode favors the HER. Hence, in order to simulate real "polarity inversion process", the values of  $\eta_{\text{lim-H}}$ , as well as  $\eta_{\text{lim-O}}$  during the cycles 2–5 should be accordingly changed, as marked with the arrows in Fig. 3a (for cycles 2–5  $\eta_{\text{lim-H}}$  should be set at  $-0.10 \text{ V}$ , while  $\eta_{\text{lim-O}}$  should be



set at 1.48 V). It is important to note that the anodic current densities at  $\eta_{\text{lim-O}}$  during all 5 cycles are much higher than that ( $j = 0.015 \text{ A cm}^{-2}$ ) predicted by procedures given in Experimental section since all CVs are placed in the region of anodic current densities.

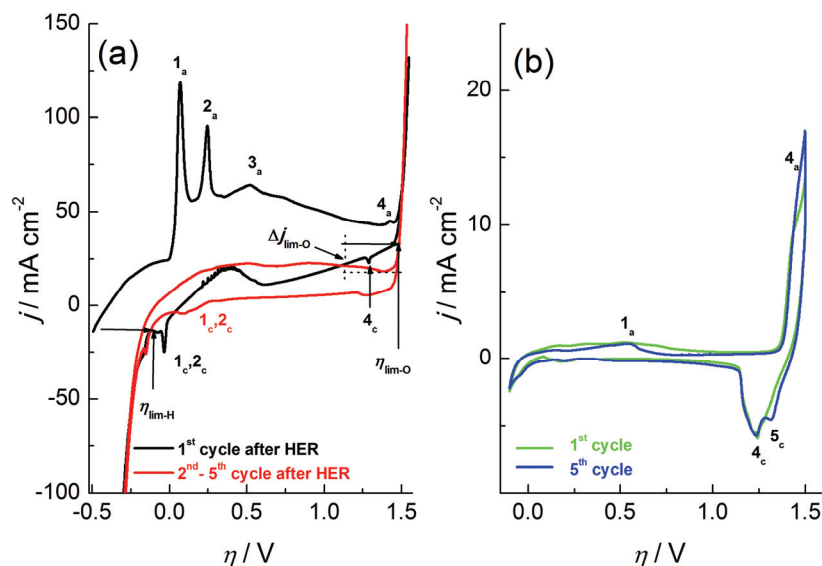


Fig. 3. 1<sup>st</sup> and 5<sup>th</sup> CV recorded at Ni 40 mesh electrode at  $\nu = 50 \text{ mV s}^{-1}$  after HER at  $j = -0.3 \text{ A cm}^{-2}$  for 5 h and after holding electrode at  $\eta_{\text{lim-H}} = -0.494 \text{ V}$  for 200 s (a) and the same CVs recorded in  $\text{N}_2$  saturated solution after holding electrode at  $\eta_{\text{lim-H}} = -0.10 \text{ V}$  for 200 s (b).

Hence, considering the results presented in Figs. 1–3 following remarks could be made: for both samples, stable overpotential responses on freshly prepared electrodes could be established after the electrolysis duration of approximately 3 h, indicating that during the first year of their operation in industrial cell (before the first “polarity inversion”) their overpotentials would be these given in Table I; for the NiSn coating the values of  $\eta_{\text{lim-H}}$  (given in Table I) could be applied for recording CVs, while the value of and  $\eta_{\text{lim-O}}$  should be corrected as presented in Fig. 3a (see Table I); in the case of Ni mesh sample  $\eta_{\text{lim-O}} = 1.55 \text{ V}$  could be used for the CVs, while  $\eta_{\text{lim-H}}$  should be set at  $-0.100 \text{ V}$ , as shown in Fig. 3b (these values are also given in Table I). It should also be emphasized that during the application of CASLT-HER the values of  $\eta_{\text{lim-H}}$  and  $\eta_{\text{lim-O}}$  might request additional correction to satisfy conditions of “polarity inver-

TABLE I. The values of  $\eta_{\text{s,HER}}$ ,  $\eta_{\text{lim-H}}$  and  $\eta_{\text{lim-O}}$  for both electrodes

Sample	$\eta_{\text{s,HER}} / \text{V}$	$\eta_{\text{lim-H}} / \text{V}$	$\eta_{\text{lim-O}} / \text{V}$
NiSn	-0.169	-0.042	1.520
Ni 40 mesh	-0.787	-0.100	1.480



sion”, since in the preliminary experiments presented in Figs. 1-5 these values were obtained only for the step (1) defined in Experimental.

### CASLT-HER

The ASLT<sup>1</sup> was designed to mimic the cathode condition during long term service in industrial chlor-alkali<sup>2-5</sup> and alkaline water electrolysis systems.<sup>1,17</sup> Since it was shown that the overpotential for the HER at Ni electrode changes with the time of electrolysis,<sup>10</sup> it was assumed that similar behavior could be expected for the NiSn and Ni 40 mesh. Accordingly, new CASLT-HER was used in this work, as described in Experimental. As shown in Fig. 1, during the first step (1) in the CASLT-HER, it was necessary to hold NiSn and Ni 40 mesh electrodes for at least 5 h at  $j = -0.3 \text{ A cm}^{-2}$  to provide stable overpotential response ( $\eta_s$ ).

*NiSn coating sample.* The  $\eta-t$  response recorded before applying cycling procedure was identical to the one presented in Fig. 1a, while  $\eta-t$  responses recorded after cycling procedures slightly changed the shape and positions, being placed at more negative overpotentials after each run of CVs. Values of  $\eta$  taken at different times (marked in the figure) from the  $\eta-t$  dependences recorded at  $j = -0.3 \text{ A cm}^{-2}$  as a function of the number of cycles are shown in Fig. 4. As can be seen  $\eta$  becomes more negative (higher) with the increase of the number of cycles, as well as with the time of electrolysis. The smallest change in  $\eta$  is recorded after 3 h of electrolysis, so that  $\eta$  recorded after 5 h of electrolysis could be used as  $\eta_s$ .

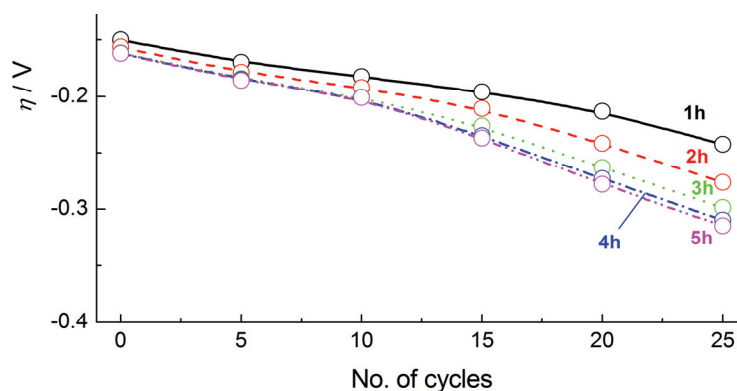


Fig. 4. Values of  $\eta$  taken at different times (marked in the figure, 1–5 h) from the  $\eta-t$  dependences recorded at  $j = -0.3 \text{ A cm}^{-2}$  for the NiSn sample.

In Fig. 5a are presented 1<sup>st</sup> cycles in each run (cycles 1, 6, 11, 16 and 21), while in Fig. 4b are shown 5<sup>th</sup> cycles in each run (cycles 5, 10, 15, 20 and 25). Characteristic peak 1<sub>a</sub> is seen only for the first cycle in each run, with its maximum decreasing with the number of cycles (Fig. 4a). Concerning the pair of peaks 2<sub>a</sub> and 2<sub>c</sub> for the reaction  $\text{Ni}(\text{OH})_2 \leftrightarrow \text{NiOOH}$ , only peak 2<sub>c</sub> is present on all

CVs, while peak  $2_a$  could be seen only for cycles 1 and 6. At the same time the current density at  $\eta_{\text{lim-O}}$  increases from 70 to 280 mA cm<sup>-2</sup> from cycle 1 to 21. On the other side, the value of  $\eta_{\text{lim-H}} = -0.042$  V produced slightly higher current density for the HER in comparison to that used to determine  $\eta_{\text{lim-H}}$  (see Fig. 1). As expected for the last cycle in each run (cycles 5, 10, 15, 20 and 25), peak  $1_a$  is not present on the CVs. The peak  $2_c$  could be seen on all CVs, while the peak  $2_a$  disappears after 15<sup>th</sup> cycle. Again, the current density at  $\eta_{\text{lim-O}}$  is seen to increase to 300 mA cm<sup>-2</sup> with the number of cycles. Hence, in accordance with a previous statement that, in order to keep the constant conditions of “polarity inversion” (the same value of  $j_{\text{lim-O}}$ ), the value of  $\eta_{\text{lim-O}}$  for recording CVs should be corrected during the cycling procedure.

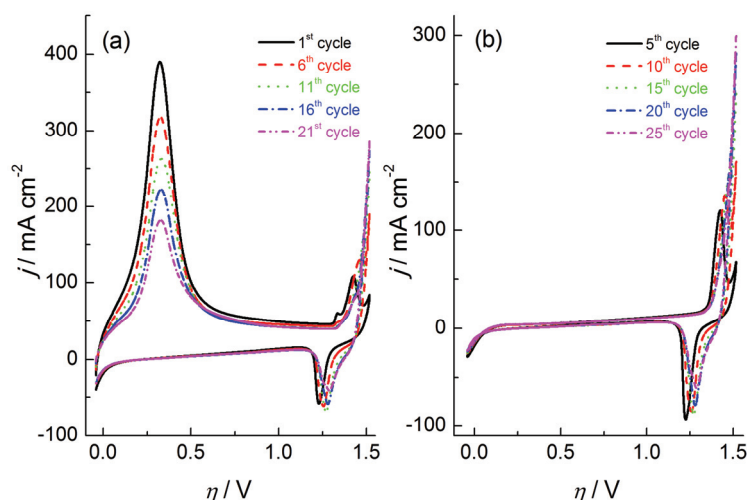


Fig. 5. 1<sup>st</sup> (a) and 5<sup>th</sup> (b) CVs recorded at NiSn electrode for each run at  $v = 50$  mV s<sup>-1</sup> after HER at  $j = -0.3$  A cm<sup>-2</sup> for 5 h and after holding electrode at  $\eta_{\text{lim-H}} = -0.042$  V for 200 s.

*Ni mesh sample.* As in the case of NiSn sample,  $\eta-t$  response recorded before applying cycling procedure was practically identical to the one presented in Fig. 1b, while  $\eta-t$  responses recorded after cycling procedures changed in the opposite direction in comparison with the NiSn electrode, being placed at less negative (lower) overpotentials after first 3 runs of CVs, indicating that the “polarity inversion” has a positive effect on the activity of Ni 40 mesh electrode towards the HER. Values of  $\eta$  taken at different times (marked in the figure) from the  $\eta-t$  dependences recorded at  $j = -0.3$  A cm<sup>-2</sup> as a function of the number of cycles for Ni 40 mesh sample are shown in Fig. 6. After 1 h of electrolysis  $\eta$  is seen to decrease from about  $-0.65$  to about  $-0.41$  V during the first 3 runs of CVs, while further change (up to 5<sup>th</sup> run) is negligible. After 2–5 h of electrolysis the change of  $\eta$  during the first 3 runs of CVs is more pronounced, reaching minimum of

about  $-0.30$  V for 5 h of electrolysis. During the 4<sup>th</sup> and 5<sup>th</sup> run of CVs the value of  $\eta$  is seen to increase, indicating that the effect of “polarity inversion” changed from positive to negative.

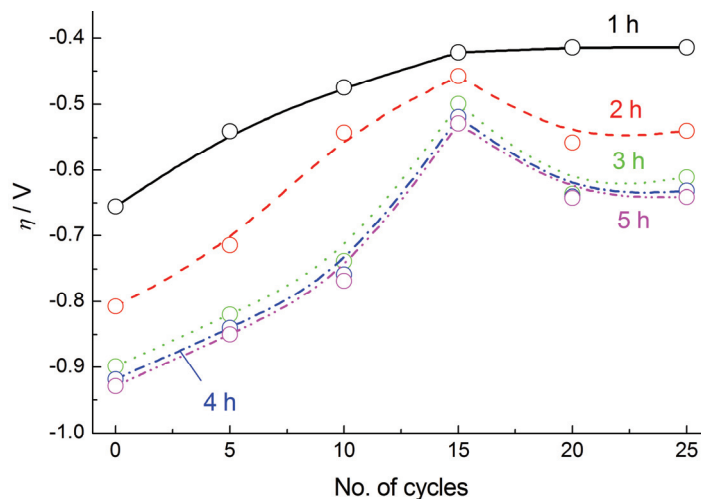


Fig. 6. Values of  $\eta$  taken at different times (marked in the figure, 1–5 h) from the  $\eta$ - $t$  dependences recorded at  $j = -0.3$  A cm<sup>-2</sup> for the Ni mesh sample.

In Fig. 7a are presented 1<sup>st</sup> cycles in each run (cycles 1, 6, 11, 16 and 21), while in Fig. 7b are shown 5<sup>th</sup> cycles in each run (cycles 5, 10, 15, 20 and 25). As can be seen the 1<sup>st</sup> cycle is practically the same as that presented in Fig. 3a, while the 1<sup>st</sup> cycles in subsequent runs are not characterized with the sharp peaks of the  $\alpha$ -NiH and  $\beta$ -NiH phases<sup>10–13</sup> dissolution. Much smaller anodic peaks, being less pronounced for subsequent runs, indicate smaller amount of the  $\alpha$ -NiH and  $\beta$ -NiH phases which practically disappear for 4<sup>th</sup> and 5<sup>th</sup> run. At the same time, the last cycles in each run are practically the same for runs 1–3, while for runs 4 and 5 only one broad anodic peak around  $\eta = 0.0$  V could be detected on the CVs, indicating that the  $\alpha$ -NiH and  $\beta$ -NiH phases might again be formed in smaller amount during long time hydrogen evolution. Such behavior is in accordance with the change of  $\eta$  as a function of the number of cycles (Fig. 6). As in the case of NiSn sample, the current density at  $\eta_{\text{lim-O}}$  is seen to increase to 62 mA cm<sup>-2</sup> with the number of cycles (Fig. 7b). Hence, the same remark as that for the NiSn sample concerning the value of  $\eta_{\text{lim-O}}$  is valid for the CVs recorded for Ni 40 mesh electrode (correction during the cycling procedure).

Considering  $\eta$ - $t$  dependences for both electrodes it could be stated that a stable overpotential response  $\eta_s$  is obtained after 4–5 h of HER at  $j = -0.3$  A cm<sup>-2</sup>. The result presented in Fig. 8 is obtained by subtracting absolute values of  $\eta_s$  for the NiSn sample from that of the Ni 40 sample, using Eq. (1):

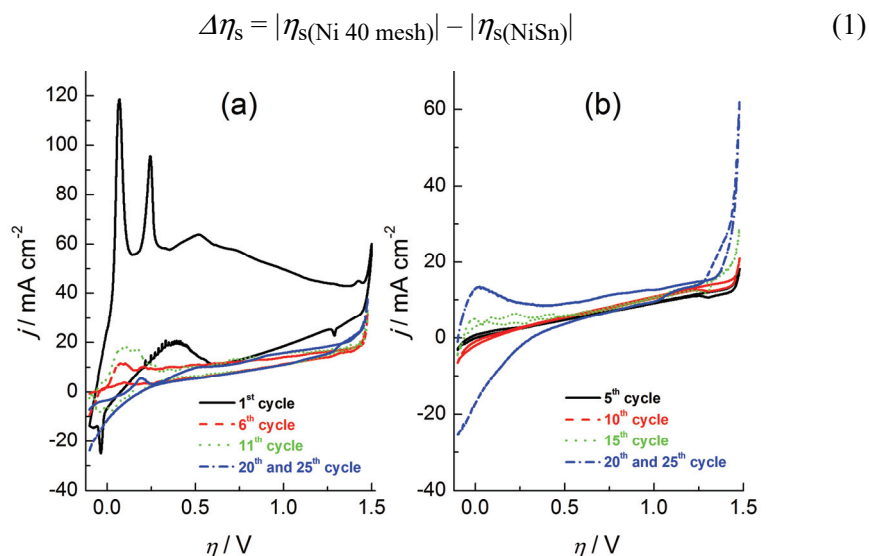


Fig. 7. 1<sup>st</sup> (a) and 5<sup>th</sup> (b) CVs recorded at Ni mesh electrode for each run at  $v = 50 \text{ mV s}^{-1}$  after HER at  $j = -0.3 \text{ A cm}^{-2}$  for 5 h and after holding electrode at  $\eta_{\text{lim-H}} = -0.1 \text{ V}$  for 200 s.

The difference between the overvoltages for the HER for these two electrodes clearly indicates the advantage of using NiSn coating instead of Ni 40 mesh electrode. This difference is the highest before the “polarity inversion”, being 0.770 V, while after first “polarity inversion” its value decreases reaching minimum of 0.30 V at 3<sup>rd</sup> “polarity inversion” (3<sup>rd</sup> year of their work in industrial cells) and continuing to work at slightly higher overpotentials for the next 2 years of exploitation.

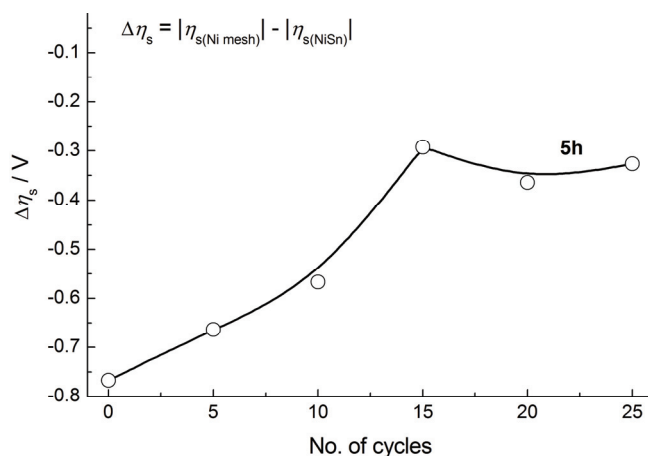


Fig. 8. The difference in overpotentials for the HER at  $j = -0.3 \text{ A cm}^{-2}$  as a function of the number of cycles.

Comparing this results with the results presented in our recent work,<sup>1</sup> it could be stated that previously published results showed better performance of NiSn electrode, which is the result of a short time for the application of  $j = -0.3 \text{ A cm}^{-2}$ , as well as the result of incorrect values of  $\eta_{\text{lim-H}}$  and  $\eta_{\text{lim-O}}$  during the application of CVs (Figs. 5 and 7 of Ref.<sup>1</sup>). It is important to note that even after correction of the values of  $\eta_{\text{lim-H}}$  and  $\eta_{\text{lim-O}}$ , the real conditions of the “polarity inversion process” were not established, particularly for the  $\eta_{\text{lim-O}}$  (the current densities at  $\eta_{\text{lim-O}}$  were much higher than predicted for both investigated electrodes), indicating that the “polarity inversion” conditions used in this work were more rigorous than predicted ones for the industrial application. Hence, it could be concluded that the value of  $\eta_{\text{lim-O}}$  should be corrected during the application of CVs, in order to establish proper conditions of “polarity inversion”.

#### *Characterization of samples by SEM analysis*

The surfaces of both samples were characterized by SEM analysis before and after the CASLT-HER.

In Fig. 9a is presented Ni 40 mesh before the CASLT-HER, while in Figs. 9b and 9c is shown Ni 40 mesh after the CASLT-HER. It is seen that its surface is much rougher after the CASLT-HER and that processes of  $\alpha$ -NiH and  $\beta$ -NiH phases formation and dissolution, as well as processes of  $\text{Ni(OH)}_2$  formation and reduction and  $\text{Ni(OH)}_2 \leftrightarrow \text{NiOOH}$  reaction caused irreversible changes on the surface of the Ni 40 mesh during the CASLT-HER, it is possible that such increase caused to some extent its activation towards the HER, but the decrease in overpotential for the HER for about 0.32 V cannot be the result of the surface roughness increase only and it is possible that during the cycling procedure some phases ( $\beta$ -NiOOH or  $\gamma$ -NiOOH) are formed, being catalysts for the HER.

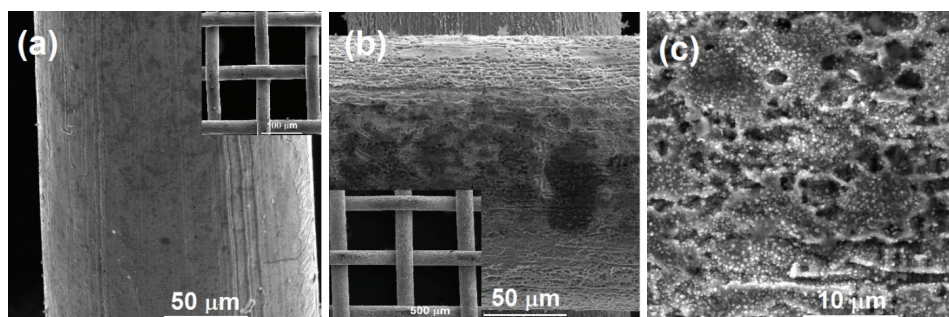


Fig. 9. a) SEM of the Ni 40 mesh before CASLT-HER. Inset: Ni 40 mesh at lower magnification. b) SEM of the Ni 40 mesh after CASLT-HER. Inset: Ni 40 mesh at lower magnification. c) SEM of the Ni 40 mesh after CASLT-HER at the highest magnification.



In the case of NiSn sample significantly higher surface area is exposed to the CASLT-HER, as shown in Fig. 10. On a freshly electrodeposited NiSn coating two types of coating could be detected: mostly cauliflower type of the coating (c) and partially honeycomb like type of the coating (d). During the CASLT-HER procedure certain parts of the coating were peeled off, mainly convex parts of the coating surface, as can be seen in Fig. 10a and b. Accordingly, the amount of meta-stable  $\text{Ni}_{(1+x)}\text{Sn}$  phase, which is responsible for the catalysis of the HER, decreased and the overpotential for the HER increased during the CASLT-HER. It is interesting to note that after the CASLT-HER (Fig. 10b), a cauliflower type of the coating disappeared and the whole surface of the sample was honeycomb like type of the coating, which is characteristic for the surfaces with extensive hydrogen evolution.

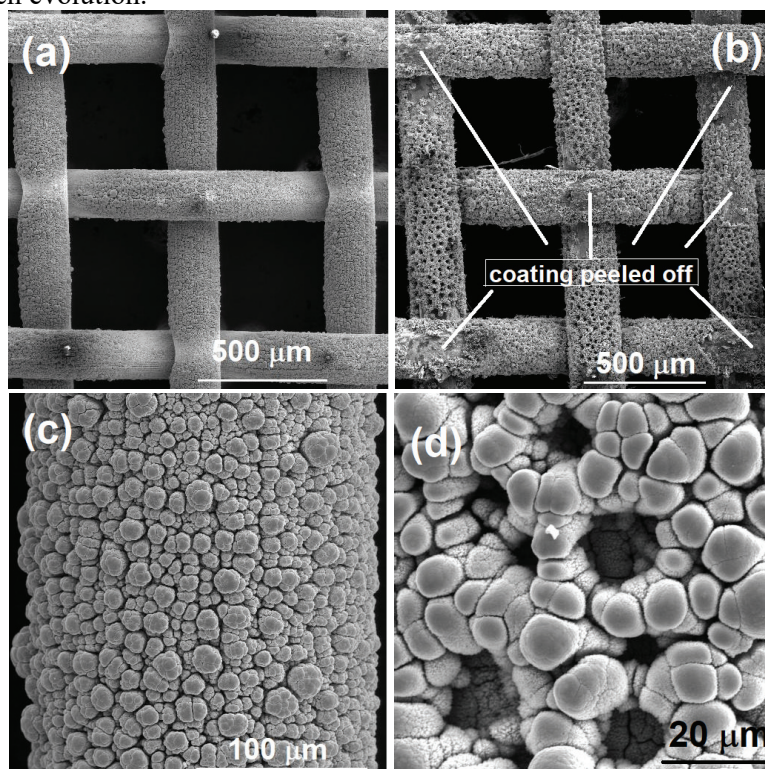


Fig. 10. a) NiSn coating before the CASLT-HER. b) NiSn coating after the CASLT-HER. c) Cauliflower type of the NiSn coating present on some parts of a freshly electrodeposited sample. d) Honeycomb-like type of the coating present on some parts of a freshly electrodeposited sample, as well as on the whole surface of the NiSn sample after the CASLT-HER.

Finally, if we compare results obtained in our recent work<sup>1</sup> with the results presented in this work, following remarks could be made: during the ASLT<sup>1</sup> the NiSn alloy coating catalytic activity for the HER decreased for about 24 mV after

25 cycles, while in this work this decrease is much higher, about 145 mV; concerning Ni 40 mesh electrode, catalytic activity for the HER was found to increase for the HER (about 103 mV) during the ASLT,<sup>1</sup> while in this work the increase amounts to 153 mV. Hence, it appears that in order to mimic the real conditions of “polarity inversion” during the service life test, investigated electrodes should be held at least 5 h at a constant current density  $j = -0.3 \text{ A cm}^{-2}$ .

#### CONCLUSIONS

Considering results presented in this work following conclusions could be made for a correct application of the service life test for both electrodes in the industrial process of alkaline water electrolysis: 1) electrodes should be held at the conditions of industrial current density for at least 5 h; 2) the limiting values for the application of CVs should be determined in a separate experiments and should be corrected during the application of this procedure; 3) comparing the overvoltages for the HER at NiSn coating and Ni 40 mesh, it is obvious that the NiSn electrode would possess from maximum 0.77 V to minimum 0.30 V better overvoltage during the 5 years of their exploitation in the industrial alkaline water electrolysis.

*Acknowledgement.* The authors are indebted to the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172054) for the financial support of this work.

#### ИЗВОД

#### КОРИГОВАН УБРЗАНИ ТЕСТ ЗА ИСПИТИВАЊЕ РАДНОГ ВЕКА ЕЛЕКТРОХЕМИЈСКИ ИСТАЛОЖЕНЕ NiSn ЛЕГУРЕ И Ni КАТОДА У УСЛОВИМА ИНДУСТРИЈСКЕ ЕЛЕКТРОЛИЗЕ ВОДЕ У АЛКАЛНИМ РАСТВОРИМА

ВЛАДИМИР Д. ЛОВИЋ,<sup>1</sup> БОРКА М. ЛОВИЋ,<sup>1</sup> НЕВЕНКА Р. ЕЛЕЗОВИЋ<sup>2</sup> И ЉИЉАНА ГАЛИЋ-КРСТАЈИЋ<sup>2</sup>

<sup>1</sup>Институт за мултидисциплинарна истраживања Универзитета у Београду, Београд и <sup>2</sup>Институт за техничке науке САНУ, Кнез Михајлова 35, 11000, Београд

Коригован убрзани тест за електрохемијско издвајање водоника (CASLT-HER), дизајниран за примену одређених електродних материјала као катода у ћелијама за електролизу воде у алкалним растворима, примењен је на електродама од електрохемијски исталожене NiSn легуре и на Ni мрежици у раствору 30 % KOH на 80 °C. Ni мрежица је благо нагизена, док је NiSn легура електрохемијски исталожена из раствора који је садржао пирофосфате, глицин, SnCl<sub>2</sub> и NiCl<sub>2</sub> на Ni мрежицу до дебљине од око 40 μm. Показано је да NiSn катоде поседују од максимум 0,77 V до минимум 0,30 V бољу пренапетост од Ni мрежице за време од 5 година њихове експлоатације у условима електролизе воде у алкалним растворима. Такође је показано да обе електроде треба испитивати при густини струје  $j = -0,3 \text{ A cm}^{-2}$  најмање 5 сати. Граничне вредности пренапетости за примену цикличне волтаметрије (симулација „инверзне поларизације“) морају бити одређене у посебном експерименту пре примене теста и морају бити прилагођаване за време примене цикличне волтаметрије.

(Примљено 15 маја, ревидирано 3. јула, прихваћено 5. јула 2019)



## REFERENCES

1. V. D. Jović, B. M. Jović, U. Č. Lačnjevac, N. V. Krstajić, P. Zabinski, N. R. Elezović, *J. Electroanal. Chem.* **819** (2018) 16 (<https://dx.doi.org/10.1016/j.jelechem.2017.06.011>)
2. A. L. Antozzi, C. vBargioni, L. Jacopetti, M. Musiani, L. Vazquez-Gomez, *Electrochim. Acta* **53** (2008) 7410 (<https://dx.doi.org/10.1016/j.electacta.2007.12.025>)
3. V. D. Jović, U. Lačnjevac, B. M. Jović, N. V. Krstajić, *Electrochim. Acta* **63** (2012) 124 (<https://dx.doi.org/10.1016/j.electacta.2011.12.078>)
4. V. D. Jović, U. Č. Lačnjevac, B. M. Jović, Lj. M. Gajić-Krstajić, N. V. Krstajić, *J. Serb. Chem. Soc.* **78** (2013) 689 (<https://dx.doi.org/10.2298/JSC120831112J>)
5. B. M. Jović, U. Č. Lačnjevac, N. V. Krstajić, V. D. Jović, *Int. J. Hydrogen Energy* **39** (2014) 8947 (<https://dx.doi.org/10.1016/j.ijhydene.2014.04.015>)
6. M.B.F. Santos, P.E. Da Silva, R. Andrade Jr, J.A.F. Dias, *Electrochim. Acta* **37** (1992) 29 ([https://dx.doi.org/10.1016/0013-4686\(92\)80007-9](https://dx.doi.org/10.1016/0013-4686(92)80007-9))
7. H. Yamashita, T. Yamamura, K. Yoshimoto, *J. Electrochem. Soc.* **140** (1993) 2238 (<https://dx.doi.org/10.1149/1.2220802>)
8. V. D. Jović, U. Lačnjevac, B. M. Jović, Lj. Karanović, N. V. Krstajić, *Int. J. Hydrogen Energy* **37** (2012) 17882 (<https://dx.doi.org/10.1016/j.ijhydene.2012.09.110>)
9. B. M. Jović, U. Č. Lačnjevac, N. V. Krstajić, V. D. Jović, *Electrochim. Acta* **114** (2013) 813 (<https://dx.doi.org/10.1016/j.electacta.2013.06.024>)
10. D. M. Soares, O. Teschke, I. Torriani, *J. Electrochem. Soc.* **139** (1992) 98 (<https://dx.doi.org/10.1149/1.2069207>)
11. N. Krstajić, M. Popović, B. Grgur, M. Vojnović, D. Šepa, *J. Electroanal. Chem.* **512** (2001) 16 doi.org/10.1016/S0022-0728(01)00590-3
12. P.W.T. Lu, S. Srinivasan, *J. Electrochem. Soc.* **125** (1978) 1416 (<https://dx.doi.org/10.1149/1.2131689>)
13. S. Trasatti, in *Electrochemical Hydrogen Technologies*, H. Wendt, Ed., Elsevier, Amsterdam, 1990, p. 104
14. H. Bode, K. Dehmelt, J. Witte, *Electrochim. Acta* **11** (1966) 1079 ([https://dx.doi.org/10.1016/0013-4686\(66\)80045-2](https://dx.doi.org/10.1016/0013-4686(66)80045-2))
15. R. S. Schrebler-Guzman, J. R. Vilahe, A. J. Arvia, *J. Electrochem. Soc.* **125** (1978) 1578 (<https://dx.doi.org/10.1149/1.2131247>)
16. F. Hahn, B. Beden, M. J. Croissant, C. Lamy, *Electrochim. Acta* **31** (1986) 335 ([https://dx.doi.org/10.1016/0013-4686\(86\)80087-1](https://dx.doi.org/10.1016/0013-4686(86)80087-1))
17. C. Valero-Vidal, I. Herraiz-Cardona, V. Perez-Herranz, A. Igual-Munoz, *Appl. Catal., B* **198** (2016) 142 (<https://dx.doi.org/10.1016/j.apcatb.2016.05.030>).