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The long time performance of catalysts usually used in the literature

ABSTRACT

In this communication the “long time operation” in characterization of catalysts for the hydrogen evolution reaction (HER) has been discussed. It has been explained that commonly used procedure in pratically all published papers is useless and that it is necessary to define “accelerated service life test” (ASLT) in order to predict the behavor of electrodes under industrial conditions. At the same time, one example for ASLT for cathodes in chlor-alkali electrolysis, obtained in our previosly published papers is presented.

Keywords: *Long time operation, industrial electrolysis, accelerated service life tests*

During the last decade in almost each paper describing the behavior of certain catalyst for certain electrochemical reaction, mostly the HER the “long time operation” was practically mandatory in order to predict their behavior (stability) during the application in industrial plant for water splitting, or chlor-alkali electrolysis. If the authors did not present such test, reviewers recommended such test. This test assumed at least 24 h of potential measurements at a current density and temperature of electrolyte used in the industrial electrolysis. If the potential of catalysts didn’t change for more than 5 % - 10 % of the initial value the test was satisfactory and the reviewers gave positive review and accordingly the paper has been published. Since the number of these publications is extremely large, none of them will be listed in the references.

It is important to note that such tests are useless for several reasons: (1) tests are usually performed in a stationary electrolyte, while in industrial application circulating electrolyte is used; (2) often, used current density is much lower than that in industrial plants; (3) process of industrial electrolysis is never continuous and is always interrupted due to different reasons (explained in a further text).

CHLOR-ALKALI ELECTROLYSIS

In order to predict stability of commercial cathodes for the HER in industrial chlor-alkali electrolysis in zero-gap membrane cell configuration, ASLT for commercial cathodes has been designed and partially disclosed in the literature [1]. The efficiency of cathodes is a result of combination of certain activity and stability at the high cathodic current densities (> - 300 mA cm^{-2}) used in industrial applications. The loss of activity and stability of cathodes during long term operation is a consequence of the so-called polarity inversion of the electrodes. This is happening during the replacement of old electrodes of an electrolyzer with new ones in the zero-gap membrane configuration cells, when anodes and cathodes in the rest of cells in the industrial plant are short-circuited, causing a reverse current flow.

Although the replacement of electrodes lasts for some time(depending on the number of eletrolyzers in the industrial plant), reverse current flow may damage the cathodes and negatively affect their activity for the HER [2]. The manufacturers can predict how often in a certain period of time such operation should be performed and, in accordance with that, design appropriate ASLT for cathodes. Such approach is missing in the literature and there are only few papers dealing with the ASLT of electrode materials promising for use in industrial electrolysis [1,3,4] which was designed by De Nora Industries [1]. The procedure is based on a sequence of galvanostatic

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polarizations in the HER range and cyclic voltammetry (CV) in a wide potential range, from hydrogen evolution as negative limit, to oxygen evolution as positive limit (simulating the conditions of polarity inversion).According to Ref. [1] ASLT procedure should simulate 5 years of cathode operation in the industrial cells (32 wt.% NaOH, 90 ^{o}C, j = -300 mA cm^{-2}) and is composed of following sequences: (1) Galvanostatic electrolysis for 30 min. at j = -300 mA cm^{-2}; (2) pseudo–steady–state current–potential curve (corrected for ohmic drop) recorded at 0.5 mV s−1 in order to determine Tafel plots, followed with EIS measurements at various potentials in the HER region; (3) A series of five cyclic voltammograms (CVs) from −1.05 V vs. Hg/HgO to 0.70 V vs. Hg/Hgo (sweep rate 10 mV s−1); (4) Galvanostatic electrolysis for 30 min. at j = -300 mA cm^{-2}; (5) Pseudo–steady–state current–potential curve and EIS, as in sequence 2; (6) Repeating sequences 1 - 5 with 10 CVs five times. In the work of Antozzi et al. [1] procedure for ASLT is slightly modified in comparison with that used in the industry (see Ref. [4]).

These procedures are designed by the industry and could be completely different. Some industries are using ASLT designed by application of much higher current density than normally used in industrial plant for certain period of time, followed by zero current for shorter time and repeating this sequence for several times. Once the sequence is finished polarization curve is recorded in a defined current density region. Such procedure should be repeated for several times in order to predict stability of catalyst for a long time period (mainly 5 years).

In this communication the most important results of ASLT for electrodeposited NiSn alloys are presented as an example for simulation of industrial process of chlor-alkali electrolysis.

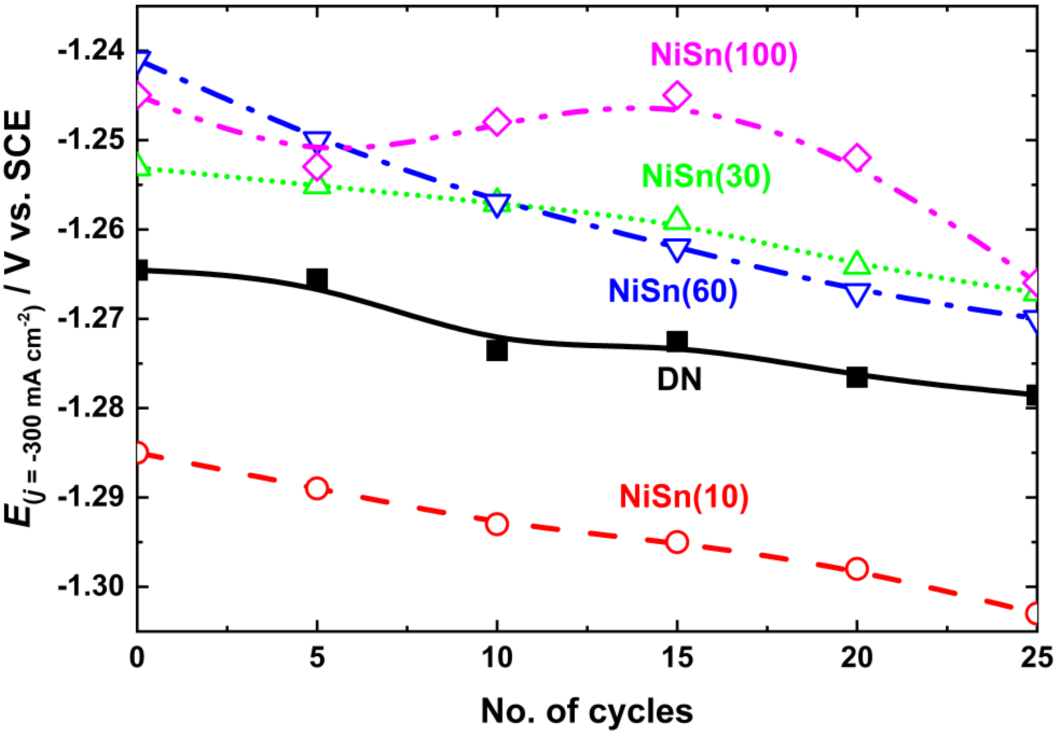

Figure 1. Dependence of E (corrected for IR drop) at j = -300 mA cm^{-2} vs. no. of cycles. (Reprinted from Ref. [6] with the permission of the Engineers Society of Corrosion, Belgrade, Serbia)

Four samples of Ni-Sn alloys were electrodeposited to a constant charge of -70 C cm^{-2}on Ni mesh 40 at constant current densities of -10 mA cm^{-2} (NiSn 10), -30 mA cm^{-2} (NiSn30), -60 mA cm^{-2} (NiSn60) and -100 mA cm^{-2} (NiSn 100) from the solution containing Ni^{2+}, Sn^{2+}, pyrophosphate and glycine [5,6]. All samples, together with the commercial De Nora (Ni-RuO_2) cathode, were submitted to the ASLT [5,6] in a stationary electrolyte under the conditions of industrial electrolysis (32 wt. % NaOH, 90 ^{o}C). Potentials recorded at j = -300 mA cm^{-2} for all investigated electrodes are presented in Figure 1 as a function of number of CVs (set of 5 CVs represent 1 year of operation in industrial cell). Hence, after 25 CVs 5 years of operation in industrial cell is simulated.

Presented results clearly show better performance of samples NiSn(30, 60 and 100) in comparison with that for the commercial De Nora cathode (DN). As it could be expected after reverse polarization (CVs) potential of all electrodes become more negative, but those for samples NiSn(30, 60 and 100) are more positive than DN for approximately 20 mV. Although this test was not performed in a circulating electrolyte, all samples were tested by the same procedure under the same conditions.

In Figure 2 are presented SEMs of NiSn(100) sample before the ASLT (a) and after the ASLT (b). As can be seen certain amounts of the NiSn coating were dissolved after the ASLT and these coatings are mainly on the convex part of the Ni mesh 40, where the cathodic and anodic current densities are higher due to different current distribution at different positions of the Ni mesh 40.

Considering presented results it could be concluded that when performing “long time performance” of catalysts it is necessary to apply the ASLT procedure in order to predict their performance in the industrial cell.

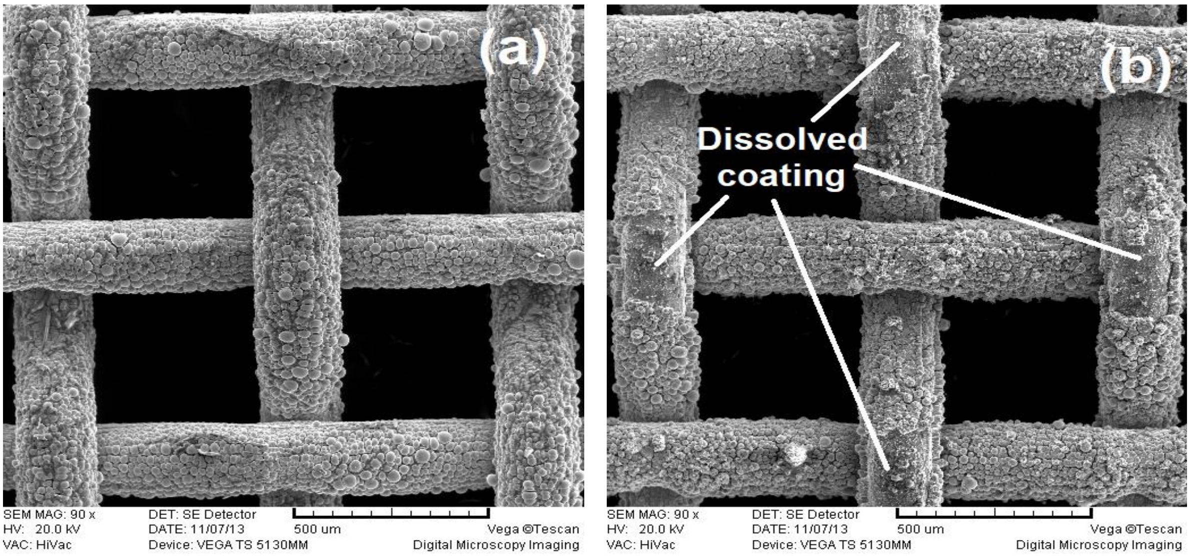

Figure 2. Appearance of the NiSn(100) coating before ASLT (a) and after the ASLT (b)

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IZVOD

PONAŠANJE KATALIZATORA PRI DUGOTRAJNOM ISPITIVANJU KOJE SE OBIČNO KORISTI U NAUČNIM RADOVIMA

U poslednjih10-ak godina u skoro svakom naučnom radu koji opisuje ponašanje određenog katalizatora u određenoj elektrohemijskoj reakciji, najčešće izdvajanje vodonika i kiseonika, tzv. "dugotrajno ispitivanje "koje traje vise od 24 sata je postalo obavezno, kako bi se predvidelo ponašanje (stabilnost) katalizatora priprimeni u industrijskom postrojenju za elektrolizu vode, ili hloralkalnu elektrolizu. U ovoj komunikaciji se govori o „dugotrajnoj operaciji" u karakterizaciji katalizatora za reakciju evolucije vodonika (HER). Objašnjeno je da je uobičajena procedura u skoro svim objavljenim radovima beskorisna i da je neophodno definisati „test ubrzanog radnog veka" (ASLT) kako bi se predvidelo ponašanje elektroda u industrijskim uslovima. Istovremeno je prikazan jedan primer za ASLT za katode u hlor-alkalnoj elektrolizi, dobijen u našim prethodno objavljenim radovima.

Ključne reči: *dugotrajno ispitivanje, ubrzani test, industrijska elektroliza*

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