Ni/Re-Co as electrocatalytic material for hydrogen evolution reaction in alkaline solution

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The electrochemical behaviour of two modified electrodes, Ni/Re$_{87}$-Co$_7$ and Ni/Re$_{57}$-Co$_{37}$ (electrodeposited Ni, covered with a thin layer of electrodeposited Re-Co alloy), was studied with respect to the hydrogen evolution reaction (HER) in a 6 M KOH solution. The data are compared with those of the pure Ni electrode. Cyclic voltammetry, polarization measurements at various current densities, and the electrochemical permeation technique of Devanathan-Stachurski were used. Kinetics parameters of HER were determined on the basis of the Tafel plots. The diffusion coefficient of permeating hydrogen and the hydrogen concentration in the electrode subsurface were calculated on the basis of permeation transients. Both modified electrodes show significantly higher values of hydrogen evolution rate and exchanged current density than those of the pure Ni electrode. The values of HER overpotential on both modified electrodes are similar, and most important is that they are much lower than the HER overpotential value on the pure Ni electrode. The hydrogen permeation data are in accordance with the voltammetric measurements. Ni electrode, modified by alloy with a lower Re content (Ni/Re$_{57}$-Co$_{37}$), shows best electrocatalytic properties with regards to HER.

Key words: electrodeposition, rhenium alloy, hydrogen evolution reaction, alkaline water electrolysis

INTRODUCTION

Hydrogen with a high purity is produced through water electrolysis, where Ni electrodes are usually employed. However, the high energy consumption is an essential disadvantage of this process. The problem can be solved by decreasing the overpotential of the cathodic and/or anodic reaction, either by an increase of the catalytic activity of the electrode or by an increase of its active surface.

The use of new materials on the base of Ni, for example alloys, is a possible way to decrease the HER overpotential. In this respect, the Ni–Co [1] and Ni-Re–Co [2] alloys are found to be effective.

The modification of Ni electrode surface with a thin layer of alloys of Co and Re could be another way for improvement of the properties of the Ni electrode. It has been found recently that HER on Ni/Re$_{87}$–Co$_7$ electrode (electrodeposited Ni, covered with a thin layer of electrodeposited Re-Co alloy with a relatively high content of Re), runs at a considerably lower overpotential in 6 M KOH

solution, compared to the pure Ni electrode [3]. Due to the high price of Re, the decrease of the amount of Re in the alloy is of great importance.

The purpose of this study is directed towards obtaining and characterization of new Ni/Re–Co electrodes with a low content of Re with respect to HER.

EXPERIMENTAL

Two types of working electrodes were obtained by electrodeposition of Re–Co alloy on one side of the electrodeposited Ni foil with a thickness of 90 μm, Ni/Re-Co with a high and with a low content of Re. For comparison, a pure Ni foil was also subjected to investigations.

The element composition of the electrodes, before and after electrochemical measurements, was determined by Energy Dispersive X-ray analysis (EDX) (JCXA 733 Jeol, Japan). The morphology of the samples was observed before and after the electrochemical measurements by Scanning Electron Microscopy (SEM) (JSM 5300, Jeol, Japan).

The electrochemical measurements were carried out in a three-electrode cell, equipped with Pt-counter electrode and Hg/HgO reference electrode.

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6 M KOH aqueous solution (analytical reagent grade) was used at a room temperature. Kinetic parameters of HER were evaluated on the basis of galvanostatic measurements at various current densities. The cyclic voltammetric dependences were obtained by scanning the potential beginning from the open circuit potential to the vertex potential in the cathodic direction, and to 800 mV in the anodic direction with a scan rate of 25 mV/s. All experiments were performed by using a potentiostat/galvanosat model of 263A (EG&G Princeton Applied Research, USA).

It was worth to investigate not only the hydrogen evolution but also the ability of the electrodes to absorb hydrogen, as well as the process of hydrogen diffusion. For this purpose, the Devanathan-Stachurski permeation technique was used [4]. The Ni/Re-Co electrode was mounted as a membrane in the cell. A thin Pd layer was electrodeposited in advance on the exit side of the membrane. Hydrogen was generated electrochemically on the entry (cathodic) side of the membrane under a galvanostatic control at $I_1 = 10$ mA/cm^2 in 6M KOH solution. 0.5 M NaOH solution was introduced into the ionization cell and 280 mV (Hg/HgO) potential was applied there. Both cells were equipped with a platinum grid as a counter electrode. At the constant positive potential, kept on the exit side of the membrane, all the hydrogen diffusing through the membrane and reaching the exit side of the membrane was oxidized. The ionization current, recorded under these conditions, was a direct measure of the hydrogen permeation rate (I_2). The permeation current was recorded against time (transient) until reaching a steady state (I_2^{st}). The I_2/I_1 relation gives the value of the permeation efficiency (I_{pe}). The values of the diffusion coefficient (D) and the concentration (C_0) of the hydrogen, absorbed into the first atomic layers of the electrode, were calculated by the equations, given in [5].

RESULTS

According to the EDX analysis, the content of both electrode systems is nearly as follows: Ni/Re$_{87}$–Co$_7$ and Ni/Re$_{57}$–Co$_{37}$. The remaining part to 100 % is oxygen.

The SEM images in Fig. 1 present the difference in the morphology of the pure Ni electrode and both Ni/Re-Co electrodes.

Pure Ni foil is characterized with a pyramidal structure, while both Ni/Re–Co electrodes show more grained structure than that of the pure Ni, which means more developed surface. The comparison between both Ni/Re–Co electrodes reveals that the Ni/Re$_{57}$–Co$_{37}$ electrode has more developed surface than the Ni/Re$_{87}$–Co$_7$ electrode. The CV curves of both modified Ni/Re-Co electrodes show a higher rate of HER, as well as a larger maximum of hydrogen desorption, compared to those of the pure Ni electrode, the effect being more evident at the electrode with a lower content of Re (Ni/Re$_{57}$–Co$_{37}$) (Fig. 2).

The positive effect of the modifying layer towards HER can be related with more developed surface of the double-layered electrodes, as well as with their higher catalytic activity.

Kinetics parameters of HER on the tested electrodes were evaluated on the basis of the Tafel plots (Fig.3).
Two different slopes are observed: first slope at a lower c.d. than 50 mA/cm^2 and second slope at a higher c.d. than 50 mA/cm^2. The corresponding values of the main parameters, characterizing HER, are given in Table 1.

It could be concluded, based on the data, that the limiting stages of HER for the three electrodes are different in the first slope range. The Volmer mechanism is valid for the pure Ni electrode according to the values of **b** (118 mV/dec) and **α** (0.5). In the case of Ni/Re$_{87}$-Co$_7$, the limiting stage
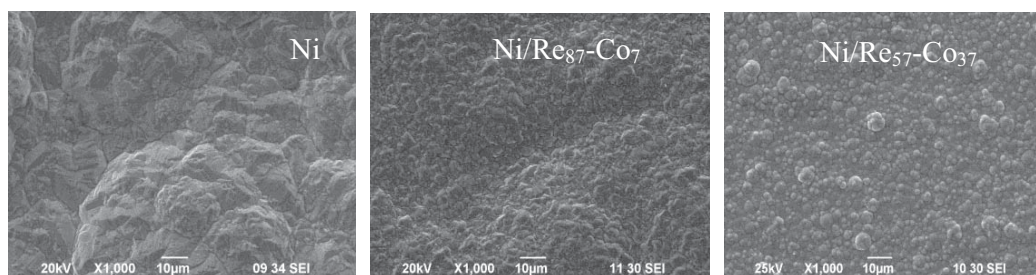

Fig. 1. SEM images of Ni, Ni/Re$_{87}$-Co$_7$ and Ni/Re$_{57}$-Co$_{37}$ electrodes.
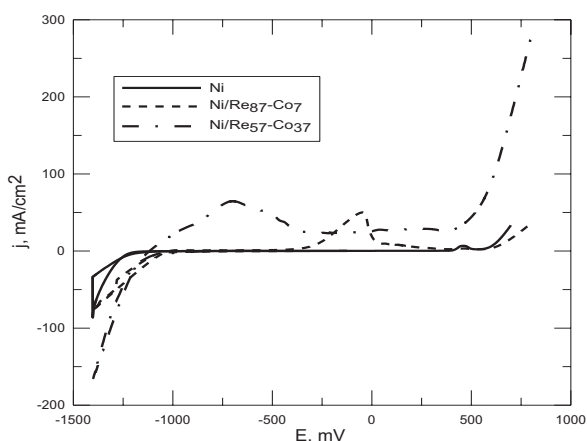
Fig. 2. CV curves of Ni, Ni/Re$_{87}$-Co$_7$ and Ni/Re$_{57}$-Co$_{37}$ electrodes.
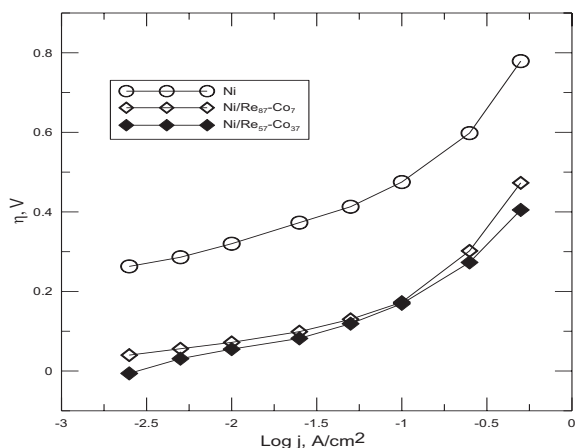
Fig. 3. Tafel plots of Ni, Ni/Re$_{87}$-Co$_7$ and Ni/Re$_{57}$-Co$_{37}$ electrodes.

Table 1. Kinetics parameters for HER on a pure Ni, Ni/Re$_{87}$–Co$_7$ and Ni/Re$_{57}$–Co$_{37}$ electrodes

Cathode material	Slope at lower cd than 50 mA/cm^2			Slope at higher cd than 50 mA/cm^2			η_{100}, mV
	b, mV/dec	i$_o$, A/cm^2	α	b, mV/dec	i$_o$, A/cm^2	α	
Ni	118	1,67*10^{-5}	0,50	428	8,39*10^{-3}	0,14	475
Ni/Re$_{87}$-Co$_7$	68	7,36*10^{-4}	0,86	424	4,17*10^{-2}	0,14	173
Ni/Re$_{57}$-Co$_{37}$	91	2,63*10^{-3}	0,64	334	3,31*10^{-2}	0,18	169

Note: η_{100} –overpotential of HER at 100 mA/cm^2

of HER is the Heyrovsky electrochemical desorption according to the values of **b** which are near to 60 mV/dec, and the values of **α** which are higher than 0.5. These are typical values of the active electrodes, dissolving a large amount of hydrogen [6]. No single rate-determining step is observed in the case of Ni/Re$_{57}$-Co$_{37}$. The second slope of the Tafel plots is characterized with **α** value, much less than 0.5, and **b** value, much higher than 120 mV, for all electrodes, i.e. the mechanism of HER is probably one and the same. Such values of **α** and **b** are explained in the literature by impurity adsorption, blocking the charge transfer [7]. It could be suggested that the hydrogen bubbles play this role prior their evolution to the electrolyte.

Both modified Ni/Re$_{87}$-Co$_7$ and Ni/Re$_{57}$–Co$_{37}$ electrodes show higher values of **i$_0$** (7. 36*10^{-4} or 2.63*10^{-3}, respectively) than that of the pure Ni electrode (1.67*10^{-5}), the difference being between one and two orders of magnitude. The values of HER overpotential on both modified electrodes are similar, and most important, they are significantly lower than the overpotential value of HER on a pure Ni electrode (η_{100} in Table 1). The values of the parameters i$_0$ and η reveal that the modification of the pure Ni electrode with a thin Re-Co layer leads to an increase of the catalytic activity towards

HER, the effect being more pronounced in the case of the Ni/Re$_{57}$–Co$_{37}$ electrode.

According to the permeation measurements (Fig. 4 and Table 2), the values of the steady state permeation rate (I$_2^{st}$) and of the permeation efficiency (I$_{pe}$) of both Ni/Re–Co electrodes are higher than those of the pure Ni electrode, the effect being more pronounced at the electrode with a low content of Re in the alloy (about 3 times).
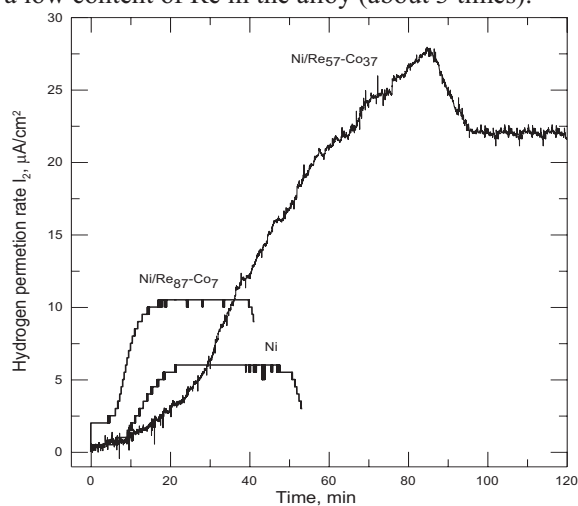

Fig. 4. Permeation transients of Ni, Ni/Re$_{87}$-Co$_7$ and Ni/Re$_{57}$-Co$_{37}$ electrodes, measured at a charging current I$_1$ = 10 mA/cm^2 and at E$_2$ = 280 mV (Hg/HgO).

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The values of C_0, corresponding to the modified Ni/Re-Co electrodes, are also higher than that of the pure Ni, and in the case of Ni/Re_{57}-Co_{37}, the C_0 value is one order of magnitude higher than that of the pure Ni electrode.

These results are in accordance with the larger maximum of hydrogen desorption in the anodic

Table 2. Steady state permeation rate (I_2^{st}), permeation efficiency (I_{pe}), diffusion coefficient (D), and concentration (C_0) of hydrogen in the subsurface layer of the Ni, Ni/Re_{87}–Co_7, and Ni/Re_{57}–Co_{37} electrodes

Cathode material	I_2^{st}	I_{pe}	D	C_0
	$\mu A/cm^2$	$\%$	cm^2/sec	Mol/cm^3
Ni	6.0	0.06	$1.5.10^{-8}$	$3.7.10^{-5}$
Ni/Re_{87}-Co_7	10.5	0.11	$2.0.10^{-8}$	$4.9.10^{-5}$
Ni/Re_{57}-Co_{37}	22	0.22	$0.5.10^{-8}$	$4.1.10^{-4}$

region of CV curves of the Ni/Re–Co electrodes (especially in the case of the Ni/Re_{57}–Co_{37} electrode), compared to the pure Ni electrode. However, the increase in the I_2^{st}, I_{pe} and C_0 in the case of modified Ni/Re–Co is not considerable, which means that it can not cause a considerable loss of hydrogen in the volume of the modified electrodes during water electrolysis.

CONCLUSION

The comparison between both modified Ni/Re–Co electrodes (with high and low Re content) and the pure Ni electrode reveals the following features:

The electrochemical behaviour, with regards to HER, is characterized with a higher rate of hydrogen evolution, higher exchange current density, and lower hydrogen overpotential in the case of the modified electrodes, the effect being more pronounced at the electrode with a lower content of Re (Ni/Re_{57}–Co_{37}). These properties of the modified electrodes can be related to their more developed surface, as well as to their higher catalytic activity. The more intensive hydrogen evolution at both modified electrodes is not accompanied with a considerable loss of hydrogen in the volume of the electrodes during the electrolysis.

The modified Ni/Co–Re electrodes could be, thereby, a promising electrocatalytic material for a negative electrode in alkaline water electrolysis. Further systematic investigations are needed in order to clarify the role of the Re in the Re–Co modifying layer, and to optimize the content of Re in the alloy with respect to the parameters of HER.

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Ni/Re-Co КАТО ЕЛЕКТРОКАТАЛИТИЧЕН МАТЕРИАЛ ЗА ОТДЕЛЯНЕ НА ВОДОРОД В АЛКАЛЕН РАЗТВОР

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(Резюме)

Изучено е електрохимичното поведение на два модифицирани електрода $Ni/Re_{87}-Co_7$ и $Ni/Re_{57}-Co_{37}$ (електроотложен никел, покрит с тънък слой електроотложена сплав Re-Co) по отношение на реакцията на отделяне на водород в разтвор на 6 M KOH. Данните са сравнени с тези на чист никелов електрод. Използвани са циклична волтамперометрия, поляризационни измервания при различни плътности на тока и електрохимичната пермиационна техника на Devanathan-Stachurski. На базата на Тафелови зависимости са определени кинетичните параметри на реакцията на отделяне на водород. На базата на пермиационните транзиенти са изчислени дифузионния коефициент на проникналия водород и концентрацията на абсорбирания водород в под-повърхностния слой на електрода. Двата модифицирани електрода показват значително по-високи стойности на скоростта на отделяне на водород и на обменния ток в сравнение с тези на чистия никелов електрод. Стойностите на свръхнапрежението на водородната реакция върху двата модифицирани електроди са подобни и най-важното, те са много по-ниски, отколкото съответната стойност върху чистия никелов електрод. Данните от пермиационните изследвания са в съгласие с волтамперометричните зависимости. Никеловият електрод, модифициран със сплав с по-ниско съдържание на Re ($Ni/Re_{57}-Co_{37}$), показва по-добри електрокаталитични свойства по отношение на реакцията на отделяне на водород.