SEAWATER ELECTROLYSIS FOR HYDROGEN PRODUCTION

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Abstract: A perspective procedure for an environmentally-clean commercial production of hydrogen by seawater as an „in situ" utilisation of marine wave generated power is the seawater electrolysis. In this paper original studies in seawater, using the methods of steady-state polarisation curves and the impedance spectroscopy were made on Ni.

Keywords: seawater electrolysis, wave energy, hydrogen, electrochemical kinetics

1. INTRODUCTION

We can estimate that in 2050 the energy demand of energy could be over twice the demand of year 2010 If the actual developing rate is maintained, about 3,4%[1,2].It is also estimated that if 0,1% of the renewable energy stored in the world seas and oceans will be converted in electric power , the world demand of energy will be five times covered by this [3].

In the actual energetic context, the proposed model is based on formulae, considered prioritaire by the European Community, but also at world level-the renewable forms of energy. The proposed model deals with capturing of a larger part from the sea waves chaotic energy, that means 2/3 of the earth surface and its direct conversion in electrical energy, in mechanical and pneumatically energy. A part of this energy could be used directly in the national electric power systems or in a world power system, and another part could be used *"in situ"* for hydrogen production.

The technology for producing hydrogen is based on the renewable energy obtained by capturing the marine waves energy [4,5], under the form of electric continuous current and using this one for sea water electrolysis, less expensive than elsewhere, because the costs are reduced at the cost of initial investment and maintenance.

In recent studies, regarding the necessity of alternative power sources development, researchers are concerned in obtaining electrical energy from marine waves and using it *in situ* for hydrogen generation by seawater electrolysis. The hydrogen kinetic was also study on stainless steel in artificial seawater [6,7]Nickel is a metal widely applied as the cathodic material in water electrolysis, due to its good catalytic activity and stability in alkaline media1and also in neutral solutions, even in seawater[2]. Recently, many studies were concerned in hydrogen evolution reaction (HER) on nickel, nickel alloys, Ni–P–titanium oxide electrodes in alkaline[8-19] and acid [20] solutions.

About the reaction mechanism, in alkaline solutions, the mainstream opinion is that atomic hydrogen is an intermediate product, the HER following the scheme[8,10,1,15-17]:

$$H_2O + M + e^- = MH_{ads} + OH^- \qquad \textit{Volmer step} \qquad (1)$$

$$MH_{ads} + H_2O + e^- = H_2 + M + OH^- \qquad \textit{Heyrovsky step} \qquad (2)$$

$$2MH_{ads} = H_2 + 2M \qquad \textit{Tafel step} \qquad (3)$$

$$MH_{ads} \rightarrow MH_{ads}^{\bullet} \qquad (4)$$

In the following is presented the investigation of kinetics of the hydrogen evolution reaction on Ni electrode in artificial seawater[8,16-19,21], using the classical steady state polarisation curves and electrochemical impedance spectroscopy. The temperature effect on steady-state polarisation curves is also investigated.

2. EXPERIMENTAL

The used electrode was an working electrode, made of a sheet of nickel of 99.9% purity with active area of 2 cm^2. Specimens were polished successively with 1000 and 1200-grade emery paper, washed with carbon tetrachloride, followed by pickling for 1 minute in a solution containing 3% HCl and washing with distilled water. A standard activation was adopted for all

specimens consisting in a cathodic polarisation at –1.2 V/SCE for 1 minute in the studied solution.

The artificial seawater was prepared using chemically pure reagents and double distilled water.(table 1). A conventional three-compartment glass cell was used. Quasi-stationary potentiostatic curves were recorded with PS 2 potentiostat, by scanning the electrode potential with 30 mV steps after 1 min. As the current reached about 100 mA, the direction of potential was reversed (backward scan).

The effect of the temperature was studied by recording the steady-state polarisation curves of Ni (forward scan) in the Tafel potential range at: 20, 30, 40, 50 and 60°C, respectively.(Table 2). The ac impedance measurements were carried out with Bas-Zahner IM6e potentiostat, controlled by a computer. Bode diagrams were obtained in the frequency range from 30 mHz to 50 kHz, at the following constant potentials: open circuit potential after cathodic activation of Ni, –1.2 and –1.3 V/SCE.

Table 1

Artificial seawater composition[17] (according to ASTM D1141)

Chemical compounds	Concentration, g/L	Chemical compounds	Concentration, g/L
NaCl	24.530	$NaHCO_3$	0.201
$MgCl_2.6H_2O$	11.103	KBr	0.101
$Na_2SO_4.10H_2O$	9.278	H_3BO_3	0.027
$CaCl_2.2H_2O$	1.539	$SrCl_2.6H_2O$	0.042
KCl	0.695	NaF	0.003

Table 2.

The values of pH in artificial seawater at various temperatures and the corresponding calculated values of the equilibrium potential, E_e, for the HER

T, K	293	303	313	323	333
pH	6.6	6.5	6.4	6.3	6.2
E_e, V/SCE	-0.624	-0.631	-0.638	-0.644	-0.650

3. RESULTS AND DISCUSIONS

The cathodic polarisation curves, obtained on Ni electrode at the temperature of 25°C in artificial seawater at forward and backward scan of the potential, are shown in Fig. 1.

The values of the exchange current density are: $i_{0,1} = 2.05x10^{-5}$ and $i_{0,2} = 7.62x10^{-6}$ A/cm^2 [10, 13-15].

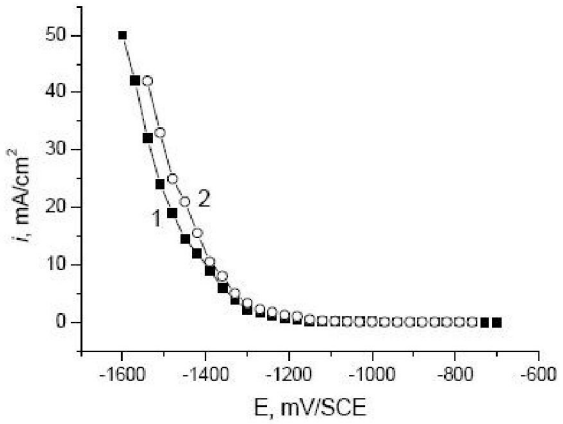

Fig. 1. Polarisation curves for HER from artificial seawater on Ni electrode at 25°C: 1-forward scan, 2- backward scan of potential

Figure 3 shows the polarisation curves for the HER within Tafel potential region on Ni in artificial seawater. The Tafel slope values increase with temperature as was expected, whereas the charge transfer coefficient decreases (Figure 3).We have noticed that the exchange current density (i_0) of the HER significantly increases with temperature (Tab. 3). Thus, at the temperature of 333 K, i_0 value is about 20 times higher than that obtained at 293 K.

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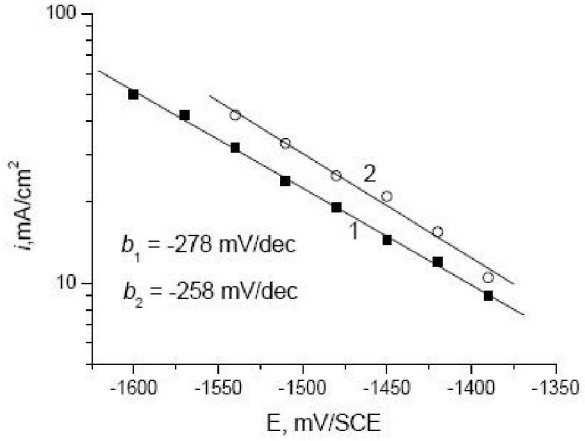

Fig. 2- Tafel lines for HER on Ni electrode in artificial seawater at 25 °C: 1-forward scan, 2- backward scan of potential

Table 3.

Electrochemical kinetics parameters of HER on Ni in artificial seawater at various temperatures

T, K	293	303	313	323	333
b, mV/dec.	-271	-317	-318	-328	-363
α	0.214	0.189	0.194	0.195	0.182
i_0*10^5, A/cm^2	1.46	9.1	9.99	14.61	27.89

The electrochemical impedance spectra in the complex plane, as Nyquist diagram and Bode plot, recorded at various potentials for Ni electrode, are shown in Fig. 4 and Fig. 5, respectively. At open circuit potential (OCP) of –0.373 V/SCE, the impedance data do not have a shape of a semicircle in the Nyquist plot (Fig. 4), suggesting a high value of corrosion resistance of Ni in artificial seawater, as shown previously.2 The Bode plot (Fig. 5) also suggests a capacitive behavior of the Ni electrode at OCP. The EIS data suggest that, in this potential region, the Tafel step may be the rate-determining step of the reaction, due to the slow diffusion of H_{ads} atoms to form H_2 molecule (reaction 3).

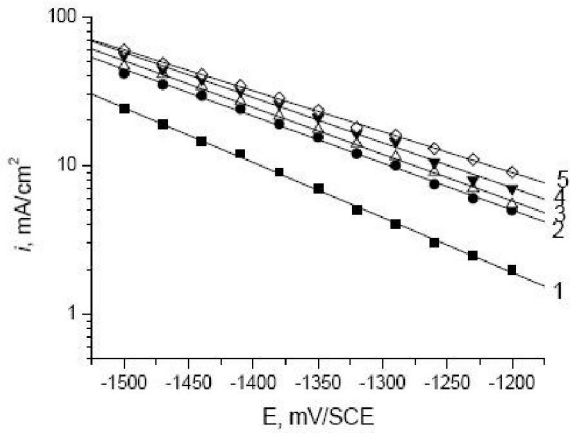

Fig. 3. Potentiostatic polarisation curves of the HER on Ni in artificial seawater in the Tafel potential region at the following temperatures: 1-293; 2-303; 3-313;4-323, 5-333 K.

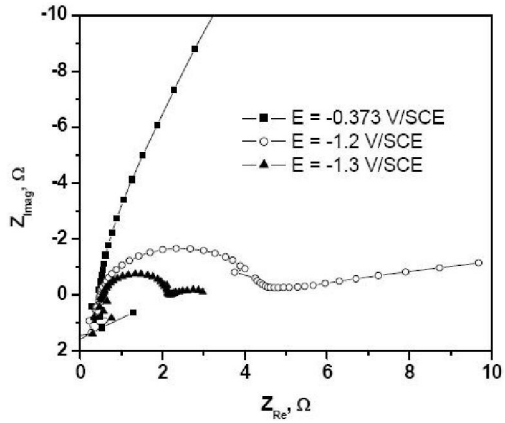

Fig. 4. Nyquist diagrams for the HER on Ni electrode in artificial seawater,recorded at temperature of 25°C and various potentials

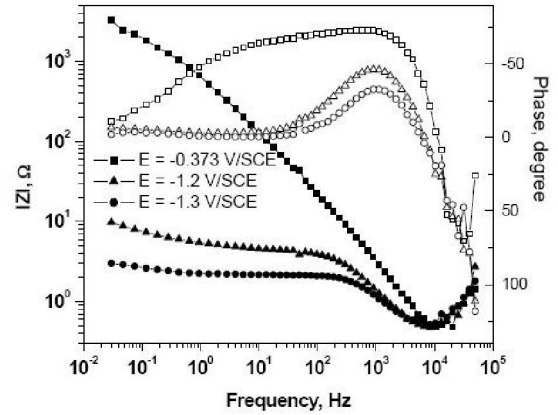

Fig. 5. Bode diagrams at Ni electrode in artificial seawater at 25°C

4. CONCLUSIONS

The nickel is corrosion resistant both in the open circuit and by polarizing in the cathodic potential region. By polarizing at potentials more cathodic than −1.2 V/SCE, the Nyquist and Bode diagrams indicate a process controlled by charge transfer step (Volmer step) and by mass transfer of the intermediate reaction product H_{ads} on electrode surface to combine in H_2 molecules (Tafel step).

A possible new energetic paradigm is based on the invention "Ecological sea electro power station" which is protected by an international copyright © AMPI 205072 and for which was submitted an invention patent request A/00840/05.10.2004. This invention was presented as a functional model al the Invention Saloon from Geneva 2005, Eureka 2005 and Pittsburgh 2006 and it has received gold medals, cups and diplomas. In the energetic actual context the proposed model is oriented towards formulae considered prioritary both at EU and world level, respectively of renewable energies [5].

The proposed model deals with capturing of a larger part from the sea waves chaotic energy, and its direct conversion in electrical energy, in mechanical and pneumatically energy and later into electrical energy and hydrogen. Such an electro power station may be executed in any ocean or sea, it is able to run continuously and can provide electrical energy and hydrogen with no additional fuel consumption.

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