

# TEMPERATURE EFFECT ON KINETICS OF THE HYDROGEN EVOLUTION REACTION

Gabriela Elena BADEA<sup>a</sup>, Alina CARABAN<sup>b</sup>, Camelia PORUMB<sup>c</sup>,  
Georgeta GAVRIS<sup>b</sup>, Oana STANASEL<sup>b</sup>

<sup>a</sup>*Faculty of Energy Engineering , University of Oradea, University St, No 1,Romania, [gbadea@uoradea.ro](mailto:gbadea@uoradea.ro)*

<sup>b</sup>*Faculty of Science, University of Oradea, University St, No 1,Romania,*

<sup>c</sup>*Faculty of Fine Arts, University of Oradea, University St, No 1,Romania,*

**Key words:** seawater, electrolysis, hydrogen, kinetics.

**Abstract.** The hydrogen evolution reaction at a stainless steel electrode in seawater has been studied at various temperatures using potentiostatic steady state voltammetry method. The effect of temperature on the kinetics parameters – exchange current density,  $i_0$  and charge transfer coefficient,  $\alpha$  - was evaluated. The formal electrochemical and chemical enthalpies of activation and the potential at which the hydrogen evolution reaction occurs as an activationless process are deduced.

## Introduction

Hydrogen generation by seawater electrolysis using electricity obtained from regional sources and its subsequent use in fuel cells is one means of reducing environmental pollution resulting from power production based on conventional technologies.

In order to produce hydrogen by seawater electrolysis, two key materials are needed: active cathodes for hydrogen evolution during seawater electrolysis, and anodes which effectively evolve oxygen instead of chlorine, even in seawater electrolysis. Platonic metals have the highest activity for the hydrogen evolution reaction [1], but they cannot be used for large scale hydrogen production. In the last decade, other cathodic materials have shown promise for hydrogen generation, including nickel and a large variety of Ni alloys: Ni [2-5], Ti-Ni alloys [6],  $Zr_{0.5}-Ti_{0.5}-V_{0.6}-Cr_{0.2}-Ni_{1.2}$  alloy [7], Ni-Mo alloys [8-9], Ni-Fe-C alloys [10], and composite materials such as Ni-P-TiO<sub>2</sub>-Ti [11].

Stainless steel is generally considered corrosion-resistant in sea water, and our studies confirmed that 18Cr-10Ni stainless steel shows corrosion resistance in sea water both under open circuit conditions, when it became spontaneously passive [12], and as a cathode when it is electrochemically protected. Moreover, the principal elements in stainless steel (Fe, Ni and Cr) are excellent catalysts for hydrogen evolution, and are second only to platinum group metals [1]. These are the reasons for use of 18Cr-10Ni stainless steel as the electrode in our study of the HER in seawater.

The aim of this paper is to investigate the kinetics, mechanism of the hydrogen evolution reaction on 18Cr-10Ni stainless steel electrodes in artificial seawater, with

the goal of using it as a cathode material during seawater electrolysis. The reaction has been studied at the constant temperature of 295 K, (PSV) and electrochemical impedance spectroscopy (EIS).

In this paper, using potentiostatic steady-state voltammetry, the influence of temperature on the kinetic of the HER at an 18Cr-10Ni stainless steel electrode in artificial seawater is studied.

### Experimental

The experimental studies were performed in a classical three-electrode cell with the anodic and cathodic spaces separated by a fritted glass disc. The working electrode (WE), with an exposed surface area of 2 cm<sup>2</sup>, was made from 18Cr-10Ni stainless steel with the following chemical composition: 18 wt % Cr, 10 wt % Ni, 0.04 wt % C; and 0.33 wt % Si; with the remainder comprised of Fe. The electrode was mechanically polished with 3/0 emery paper, degreased in alkaline solution and rinsed with double distilled water. The counter electrode was a platinum sheet with 4 cm<sup>2</sup> surface area. A saturated calomel electrode (SCE) connected with a Luggin capillary served as reference electrode. All potentials quoted in the paper are referred to this electrode.

Four sets of experiments – potentiostatic steady state voltammetry – were done in artificial seawater (ASTM D1141 norm<sup>17</sup>) prepared from analytical grade reagents and double distilled water. In all experiments the working electrode and counter electrode compartments were thermostated at 303, 313, 323 and 333 K, while the reference electrode, a saturated calomel electrode (SCE), was held at room temperature (297 ± 1 K).<sup>2</sup>

The cathodic polarisation curve was recorded using a stepwise technique of 30 mV/60 s in the Tafel potential domain (– 1.2 to –1.62 V vs. SCE) using a Radelkis potentiostat. The Tafel potential domain was deduced previously by recording polarisation curves on an extended range of potentials.

Data from the polarisation curves were used to determine the electrochemical energies of activation for the HER at various potentials,  $\Delta H_E^{o\#}$  and the electrochemical pre-exponential factors [ $\log i_E (1/T = 0)$ ].

Because the equilibrium potential of the HER was not established, with the 18Cr-10Ni stainless steel presenting spontaneous passivity in artificial seawater, its values were calculated as a function of solution pH. The measured pH of the solution and the calculated values of the hydrogen equilibrium potential at all the above-mentioned temperatures are presented in Table 1.

**Table 1.** Measured values of pH and calculated values of the equilibrium potential ( $E_e$ ) for the HER in artificial seawater at various temperatures.

<b>T / K</b>	<b>295</b>	<b>303</b>	<b>313</b>	<b>323</b>	<b>333</b>
pH	6.6	6.5	6.4	6.3	6.2
$-E_e / V$ vs. SCE	0.627	0.631	0.638	0.644	0.650

## Results

The Tafel lines for the HER on the 18Cr-10Ni stainless steel electrode in artificial seawater are plotted at different temperatures in Fig. 1.

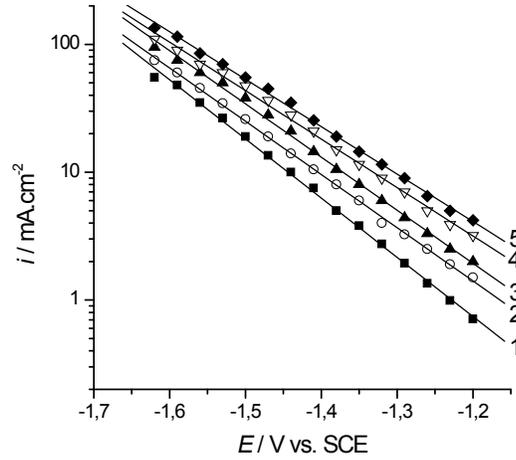


Figure 1. Tafel lines for the HER on 18Cr-10Ni stainless steel in artificial seawater as function of temperature (K): 1 – 298; 2 – 303; 3 – 313; 4 – 323; 5 – 333.

The values of the Tafel slopes ( $b$ ), of the transfer coefficients ( $\alpha$ ) and of the exchange current densities ( $i_0$ ) at each of the temperatures considered are presented in Table 2.

**Table 2.** Kinetics parameters of the HER at 18Cr-10Ni stainless steel electrode in artificial seawater at various temperatures.

$T / K$	<b>295</b>	<b>303</b>	<b>313</b>	<b>323</b>	<b>333</b>
$-b /$ $V \cdot \text{decade}^{-1}$	0.216	0.240	0.241	0.264	0.270
$\alpha$	0.27	0.25	0.26	0.24	0.24
$10^6 \cdot i_0 /$ $A \cdot \text{cm}^{-2}$	1.67	6.03	8.94	24.77	37.55

The Tafel slopes have high values, which increase with solution temperature. In addition, there is a significant increase in the exchange current density of the HER with temperature increasing. For a temperature increase from 295 to 333 K  $i_0$  increases by a factor of 20 (see Table 2).

Formal Arrhenius plots in  $\log i_E - T^{-1}$  coordinates, at constant potentials situated in Tafel region of the polarisation curves, are presented in figure 2.

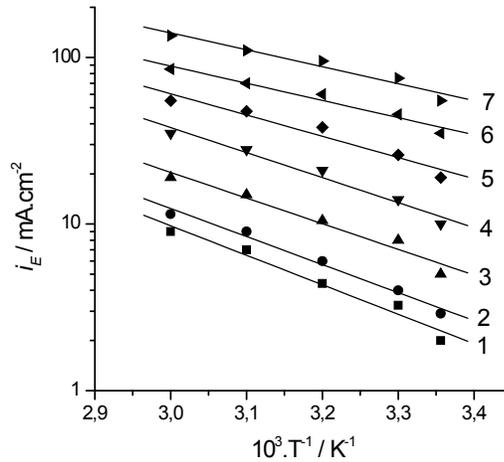


Fig.2. Plots of  $\log i_{(E)} - T^{-1}$  for the HER at 18Cr-10Ni stainless steel in artificial seawater taken at constant potentials (V vs. SCE): 1)  $-1.28$ ; 2)  $-1.32$ ; 3)  $-1.38$ ; 4)  $-1.44$ ; 5)  $-1.50$ ; 6)  $-1.56$ ; 7)  $-1.62$  within the Tafel region of the polarization curves in figure 1.

The values of the electrochemical activation enthalpy ( $\Delta H_E^{o\#}$ ) for the HER in the studied system, together with the corresponding intercepts at the ordinate axes (or electrochemical pre-exponential factors, ( $\log i_E(1/T = 0)$ ) calculated for all plots in Fig. 2 are presented in Table 3.

**Table 3.** Electrochemical Arrhenius parameters for the HER at 18Cr-10Ni stainless steel electrode in artificial seawater, at various potentials within Tafel region

$-E / \text{V vs. SCE}$	<b>1.28</b>	<b>1.32</b>	<b>1.38</b>	<b>1.50</b>	<b>1.56</b>	<b>1.62</b>
$\Delta H_E^{o\#} / \text{kJ.mol}^{-1}$	33.87	32.21	29.49	24.41	19.76	19.44
$\log i_E(1/T = 0) / \text{A.cm}^{-2}$	3.29	3.14	2.93	2.61	2.05	2.19

The electrochemical activation enthalpy of the HER on 18Cr-10Ni stainless steel in artificial seawater has only moderate values that decrease as the potential is shifted toward more negative values. Similar values and the same behaviour were reported for the HER on a Ni electrode by Kristajić *et al.*[3] in alkaline solution and by Badea *et al.*[5] in seawater.

## Discussion

**Charge transfer coefficient.** The Tafel slope parameter  $b$ , conventionally is written as  $b = RT/\alpha F$ , where  $\alpha$  is transfer coefficient, generally considered having a constant value equal with 0.5. The experimental values of  $\alpha$  show a temperature dependence (Fig.3), confirming the form for  $b$  suggested by Conway [13] for the HER at solid state electrodes; i.e.,  $b = RT/(\alpha_H + \alpha_S T)$ , where  $\alpha_H$  is the 'enthalpic'

component, being  $T$ -independent and corresponding to the conventional behaviour and  $\alpha_S$  the 'entropic' component, giving the temperature dependence of the transfer coefficient. The obtained values are:  $\alpha_H = 0.48$  and  $\alpha_S = -7.4 \cdot 10^{-4} \text{ K}^{-1}$ .

$\Delta H_E^{o\#} - E$  dependence. The dependence of the electrochemical activation enthalpy for the HER on potential,  $\Delta H_E^{o\#} - E$ , is linear (Fig.4), having a slope of  $46.55 \text{ kJ} \cdot \text{V}^{-1} \cdot \text{mol}^{-1}$  (or  $46.55 \cdot 10^3 \text{ C} \cdot \text{mol}^{-1}$ ). According to the theory [13] this slope is equal to  $-\alpha_H F$ . So, the temperature independent part of the transfer coefficient for the HER calculated from the line slope of the  $\Delta H_E^{o\#} - E$  is  $\alpha_H \cong 0.47$ , that is practical the same with the value of  $\alpha_H = 0.48$ , obtained from the temperature dependence of the charge transfer coefficient (Fig. 3).

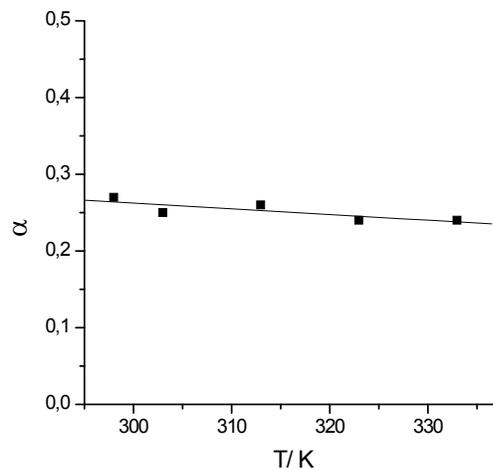


Figure 3. Conway plot of the transfer coefficients dependence of temperature for the HER on 18Cr-10Ni stainless steel electrode in artificial seawater.

From the extrapolation of the straight line with the slope  $\alpha_H F$  (Fig. 4) to  $E = 0 \text{ V}$ , the potential independent part of the electrochemical activation energy [3] is obtained, i.e. the part of the energy of activation independent of potential for the HER:  $\Delta H_E^{o\#} (E = 0) = 94.2 \text{ kJ mol}^{-1}$ . This parameter can be considered, as a measure of the electrocatalytic propriety of the electrodic material in the same solution for the investigated reaction [3, 14].

*Dependence of  $\log i_E(1/T = 0) - E$ .* Dependence of the electrochemical pre-exponential factor on the potential is presented in Fig.5. A linear relation  $\log i_E(1/T = 0) - E$  was obtained of which slope is equal to  $3.16 \text{ V}^{-1}$ . According to the theory [13] this slope is equal to  $-(\alpha_S F)/R$ , where  $\alpha_S$  is the temperature dependent part of the charge transfer coefficient for the HER. The calculated value of  $\alpha_S$  is  $-2.7 \cdot 10^{-4} \text{ K}^{-1}$ , which is reasonably close to the value of  $-7.4 \cdot 10^{-4} \text{ K}^{-1}$ , obtained from the temperature dependence of the charge transfer coefficient for the HER (Fig. 3).

By proceeding similarly as in Fig.4, through the extrapolation of the

$\log i_E(1/T=0) - E$  line with the ordinate at  $E = 0$  [Fig.5], part of the pre-exponential factor independent of potential is obtained as  $\log i_{E=0}(1/T=0) = 7.32$ . This intercept at the ordinate axis is theoretically related to the entropy of activation of the HER [3, 15].

*Ultimate enthalpy electrode potential,  $E_{H,u}$ .* The Tafel lines (Fig.1) are not parallel, they tend to cross at some potential,  $E^*$  (or overpotential,  $\eta^*$ ), so that  $i_E$  is then independent of T, i.e.  $\Delta H_{E^*}^{o\#} = 0$ . This evidently corresponds to the condition of activationless discharge considered by Krishtalik [15]. The  $E^*$ potential, named the *ultimate enthalpy electrode potential,  $E_{H,u}$* , i.e. the potential when the reaction should occur as an activationless process, is determined by intercept of the linear  $\Delta H_E^{o\#} - E$  dependence (Fig.4) with the abscissa axis (i.e.  $\Delta H_E^{o\#} = 0$ ).

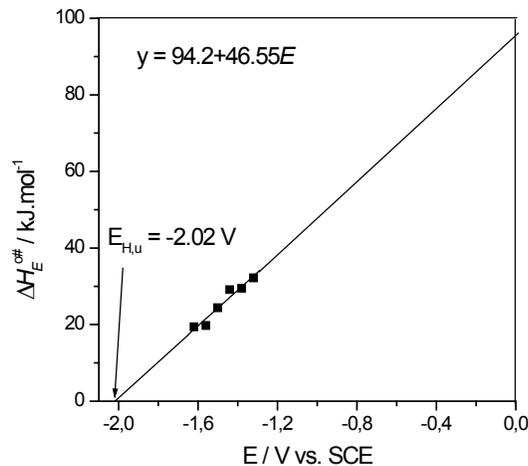


Figure 4. Dependence of  $\Delta H_E^{o\#} - E$ , for the HER at 18Cr-10Ni stainless steel in artificial seawater.

According to Fig.4 the value of the final electrode potential of the enthalpy is equal to  $-2.02$  V vs. SCE, i.e. the potential at which the HER rate on 18Cr-10Ni stainless steel in artificial seawater must be independent of the potential.

Finally another boundary property of the HER, *the ultimate entropy potential,  $E_{S,u}$* , can be found from the linear dependence  $\log i_E(1/T=0) - E$  (Fig. 5), for the particular condition:  $\log i_E(1/T=0) = 0$ . The straight line intercept with the abscissa axis is performing at the potential value of  $E_{S,u} = -2.316$  V vs. SCE.

According to Conway [6], an electrode reaction can be considered as a process without activation when both conditions  $E < E_{H,u}$  and  $E < E_{S,u}$  are satisfied. Conform to the obtained results in this paper the HER on 18Cr-10Ni in artificial seawater is an activationless process at  $E < -2.316$  V vs. SCE.

## Conclusions

The potentiostatic steady state voltammetry experiments were done for the hydrogen evolution reaction (HER) in artificial seawater at five temperatures: 298, 303, 313, 323 and 333 K. The effect of temperature on the kinetics parameters –

exchange current density,  $i_0$  and charge transfer coefficient,  $\alpha$  - was evaluated. It found that  $\alpha$  decreases and  $i_0$  increases with temperature of the solution. The formal electrochemical enthalpies of activation and the corresponding pre-exponential factors were determined. The potential at which the HER occurs as an activationless process are deduced. The values of the kinetics parameters for HER obtained are nearly close of these reported in literature data for Ni electrode in alkaline solution, that means that 18Cr-10Ni stainless steel can be used as cathode for seawater electrolysis, if the scale of the electrode surface is solved.

## References

- [1]. S. Trasatti, *J. Electroanal. Chem.*, **1972**, 39, 163-184.
- [2]. N. Krstajić, M. Popović, B. Grgur, M. Vojnović, D. Šepa, *J. Electroanal. Chem.*, **2001**, 512, 16-26.
- [3]. N. Krstajić, M. Popović, B. Grgur, M. Vojnović, D. Šepa, *J. Electroanal. Chem.*, **2001**, 512, 27-35.
- [4]. C. Hitz, A. Lasia, *J. Electroanal. Chem.*, **2001**, 500, 213-222.
- [5]. G. E. Badea, I. Maior, A. Cojocar and I. Corbu, *Rev. Roum. Chim.*, **2007**, 52, 1123-1130.
- [6]. N.V. Krstajić, B.N. Grgur, N.S. Mladenović, M.V. Vojnović, M.M. Jaksić, *Electrochim. Acta*, **1997**, 42, 323-330.
- [7]. S. Rodrigues, N. Munichandraiah, A.K. Shukla, *Bull. Mater. Sci.*, **2000**, 23, 383-391.
- [8]. M.R. Gennero de Chialvo, A.C Chialvo, *J. Electroanal. Chem.*, **1998**, 448, 87-93.
- [9]. A. Kawashima, E. Akiyama, H. Habazaki and K. Hashimoto, *Mater. Sci. Engng.*, **1997**, A 226-228, 905-913.
- [10]. S. Meguro, T. Sasaki, H. Katargiri, H. Habazaki, A. Kawashima, T. Sakaki and K. Hashimoto, *J. Electrochem. Soc.*, **2000**, 147, 3003-3011.
- [11]. B. Losiewicz, A. Budniok, A. Lasia and E. Lagiewka, *Polish J. Chem.*, **2004**, 78, 1457-1476.
- [12]. A. Cojocar, G. E. Badea, I. Maior and T. Badea, *Cor. Prot. Anticor.*, **2007**, 2, 40-46.
- [13]. B. E. Conway, in B. E. Conway, R. E. White J. O'M. Bockris (Eds.), "*Modern Aspects of Electrochemistry*", Plenum Press, New York, **1985**, vol. 16, Ch.2.
- [14]. D. B. Sepa, in J. O'M. Bockris, B. E. Conway, R. F. White (Eds.), "*Modern Aspects of Electrochemistry*". Plenum Press, New York, **1996**, vol. 29, Ch.1
- [15]. L.I. Krishtalik, *Electrokhimiya*, 6, **1970**, 507.