

# KINETICS OF THE HYDROGEN EVOLUTION REACTION ON 18Cr-10Ni STAINLESS STEEL IN SEAWATER. II. INFLUENCE OF TEMPERATURE

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The potentiostatic steady state voltammetry and electrochemical impedance spectroscopy experiments were done for the hydrogen evolution reaction in artificial seawater at five temperatures: 295, 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 impedance data was analyzed by a non-linear least square (NLS) fitting program and impedance parameters were 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

In Part I<sup>1</sup> of this paper, the kinetic of the hydrogen evolution reaction (HER) on an 18Cr-10Ni stainless steel in artificial seawater at 295 K temperature was investigated by potentiostatic steady state voltammetry (PSV) and electrochemical impedance spectroscopy (EIS) methods. The reaction was charge-transfer controlled; it showed a Tafel behaviour and clearly semicircular Nyquist impedance diagrams within the Tafel potential region (-1.2 to -1.62 V). The high Tafel slope obtained and the chemical rate constant values, calculated for the Heyrowsky step, lead to the assumption that the reaction mechanism is a consecutive combination of the Volmer step followed by the rate-determining Heyrowsky step.

In this paper, using the same experimental technique as described previously,<sup>1</sup> the influence of temperature on the kinetic of the HER at an 18Cr-10Ni stainless steel electrode in artificial seawater is studied.

## EXPERIMENTAL

Four sets of experiments – potentiostatic steady state voltammetry (PSV) and electrochemical impedance spectroscopy (EIS) – were done in artificial seawater. 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 ( $297 \pm 1$  K).<sup>2</sup>

The cell, chemicals, electrodes, pre-treatment of the working electrode and technique of measurements have been described in detail in Part I of this work.<sup>1</sup> Data on the kinetics of the HER at 295 K, previously obtained by identical experimental techniques, are used for comparison and in discussion of the results in this paper.

Data from the polarisation curves were used to determine the electrochemical energies of activation for the HER at various potentials,  $\Delta H_E^{o\ddagger}$  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.

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Table 1

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

$T / \text{K}$	295	303	313	323	333
pH	6.6	6.5	6.4	6.3	6.2
$-E_e / \text{V vs. SCE}$	0.627	0.631	0.638	0.644	0.650

## RESULTS

### 1. PSV data

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

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 Fig. 2. 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.

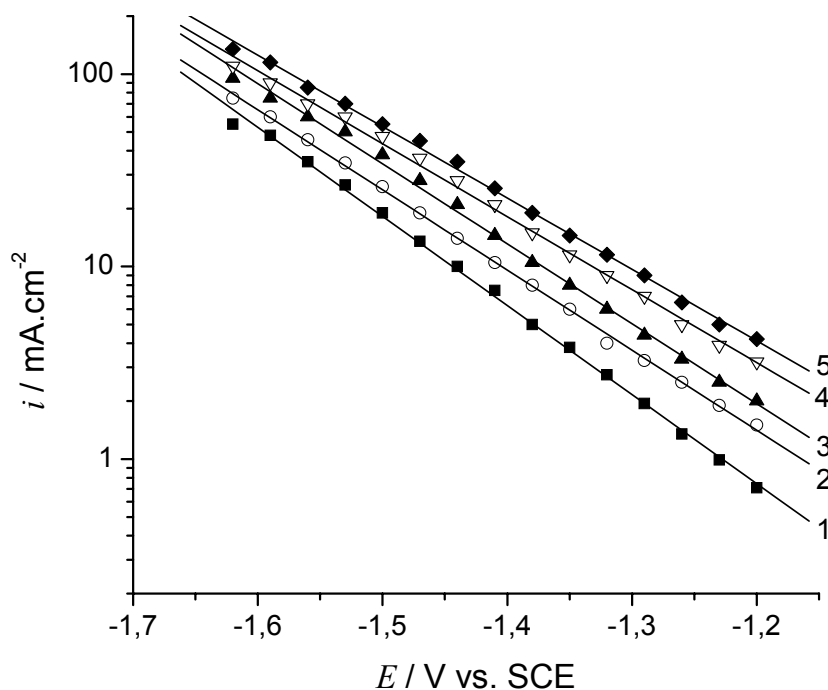


Fig. 1 – Tafel lines for the HER on 18Cr-10Ni stainless steel electrode in artificial seawater at various temperatures (K): 1 – 295; 2 – 303; 3 – 313; 4 – 323; 5 – 333.

Table 2

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

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

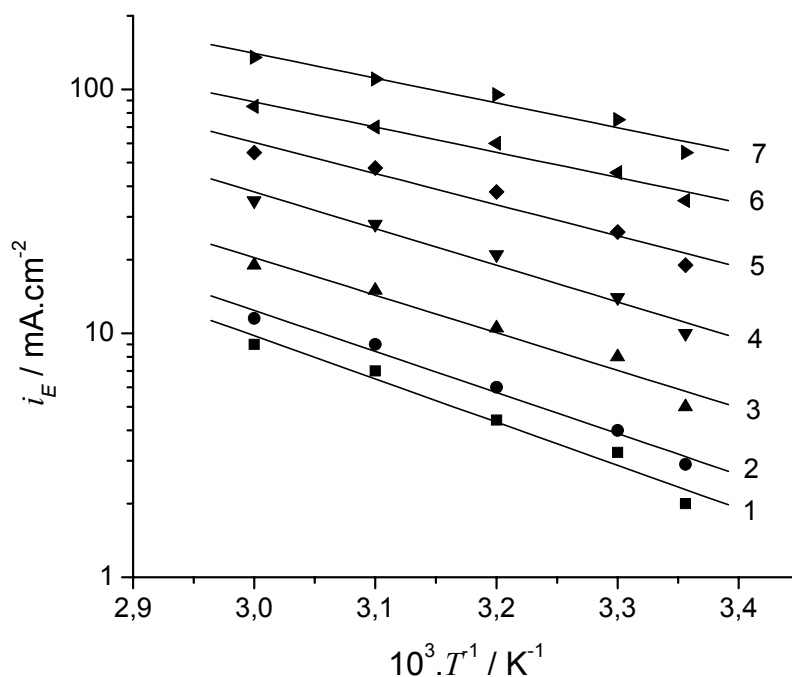


Fig. 2 – Plots of  $\log i_E - T^{-1}$  for the HER at 18Cr-10Ni stainless steel electrode in artificial seawater taken at constant potentials (V vs. SCE): 1) -1.28; 2) -1.32; 3) -1.38; 4) -1.44; 5) -1.50; 6) -1.56; 7) -1.62.

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.*<sup>2</sup> in alkaline solution and by Badae *et al.*<sup>3</sup> in seawater.

## 2. EIS data

The experimental electrochemical impedance spectra of the 18Cr-10Ni stainless steel electrode in artificial seawater at a constant potential of -1.281 V vs. SCE, taken from the Tafel region of the HER polarisation curves and at various temperatures, are presented as Nyquist and Bode diagrams in Fig. 3. The diagrams confirm the charge transfer controlled kinetics and show, as

expected, a decrease of the charge transfer resistance for the HER with solution temperature.

Fig. 4 shows the Bode form of the theoretical curves (solid lines) and experimental data (points) at -1.281 V vs. SCE and various temperatures, obtained from NLS fitting procedure, using the equivalent circuit shown in Part I<sup>1</sup> of this paper. The theoretical curves agree well with the experimental data (except for the low frequency domain, especially for the phase angle curves at high temperatures).

The experimentally-obtained impedance parameters are given in Table 4. The values of the solution resistance ( $R_s$ ) are initially high, and decrease with increasing temperature. The charge transfer resistance ( $R_{ct}$ ) decreases significantly with temperature increasing. The double layer capacitance ( $C_{dl}$ ) and the pseudo-capacitance ( $C_p$ ) increase with the increased temperature. The very large value of the pseudo-resistance ( $R_p$ ), may be

related to the chemical scaling of the electrode surface<sup>4,5</sup> process experimentally observed especially at the high temperatures. The production of  $\text{OH}^-$  ions, according to Volmer and Heyrowsky

steps (Part I<sup>1</sup>), led to an increase in pH near the electrode which allowed  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  to be precipitated as a solid phase on the electrode.

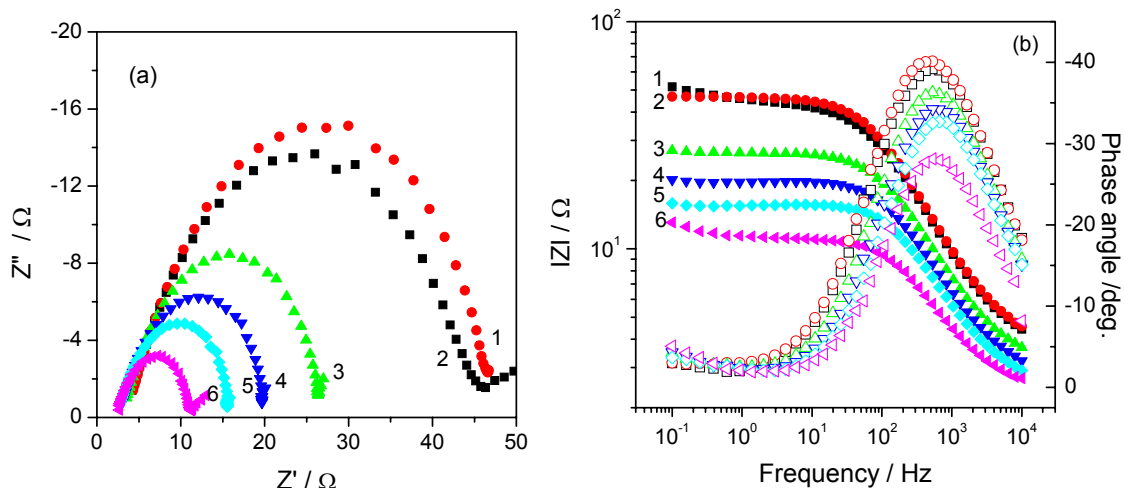


Fig. 3 – Experimental Nyquist (a) and Bode (b) diagrams for the HER on 18Cr-10Ni stainless steel electrode in artificial seawater at constant potential (-1.281 V/SCE) and various temperatures (K): 1) 295; 2) 298; 3) 303; 4) 313; 5) 323; 6) 333.

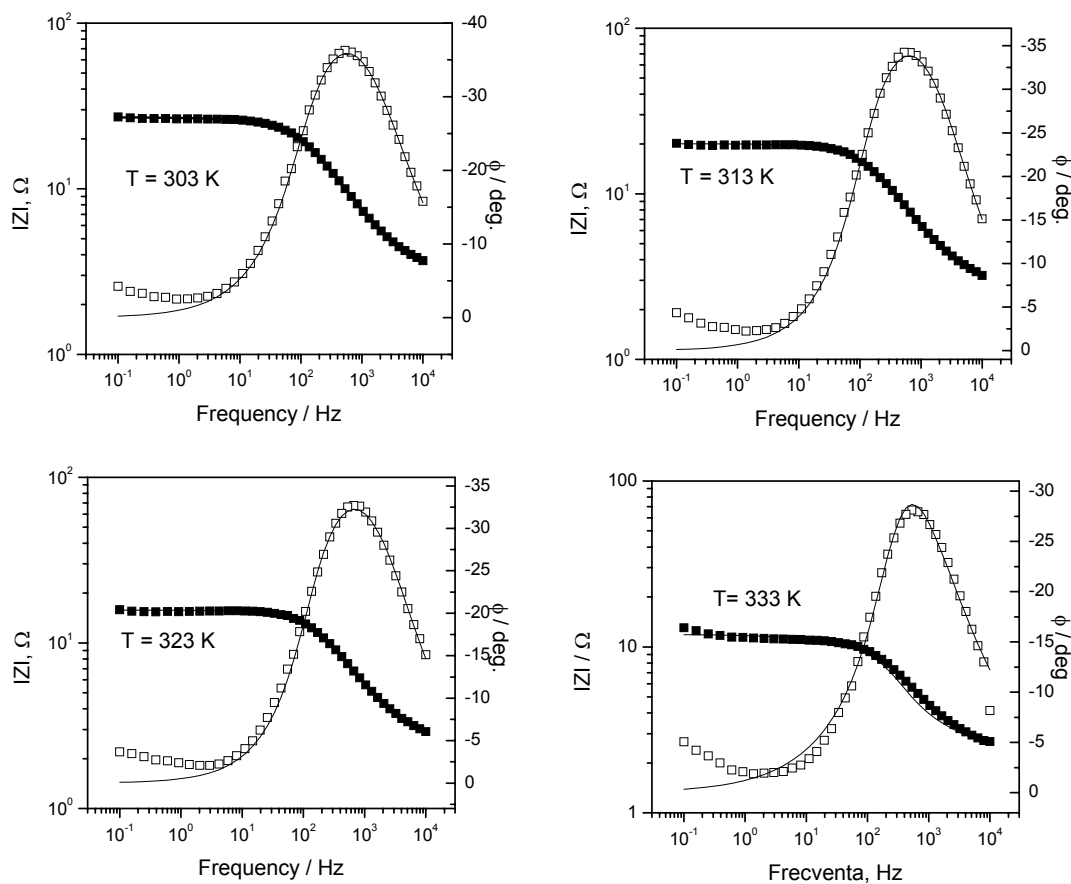


Fig. 4 – Electrochemical impedance spectra in Bode form for the HER at 18Cr-10Ni stainless steel electrode in artificial seawater at constant potential (-1.281 V/SCE) and various temperatures. The experimental data are shown as symbols and the theoretical data obtained from NLS fit results are shown as solid curves.

Table 4

Impedance parameters of the equivalent circuit for the HER at 18Cr-10Ni stainless steel electrode in artificial seawater, at the constant potential,  $E = -1.281$  V vs. SCE and various temperatures

$T /$ <b>K</b>	$R_s /$ <b><math>\Omega</math></b>	$C_{dl} /$ <b><math>\mu\text{F}\cdot\text{cm}^{-2}</math></b>	$R_{ct} /$ <b><math>\Omega\cdot\text{cm}^2</math></b>	$C_p /$ <b><math>\text{mF}\cdot\text{cm}^{-2}</math></b>	$10^{-20} \cdot R_p$ <b><math>\Omega\cdot\text{cm}^2</math></b>
303	3.2	117	48	332	2
313	2.8	126	36	432	0.37
323	2.6	132	26	599	2
333	2.4	219	18	597	2

The charge transfer resistances obtained by the EIS method at the five temperatures considered and at constant potential of  $-1.281$  V vs. ECS, plotted in coordinates  $\log(R_{ct})_E^{-1} - T^{-1}$  and approximated with linear line are presented in Fig. 5. The electrochemical energy of activation was calculated from the slope of this line. The value found is  $33.73 \text{ kJ}\cdot\text{mol}^{-1}$ , which is close to the value obtained from the Tafel lines at the potential of  $-1.28$  V vs. SCE (see Table 3).

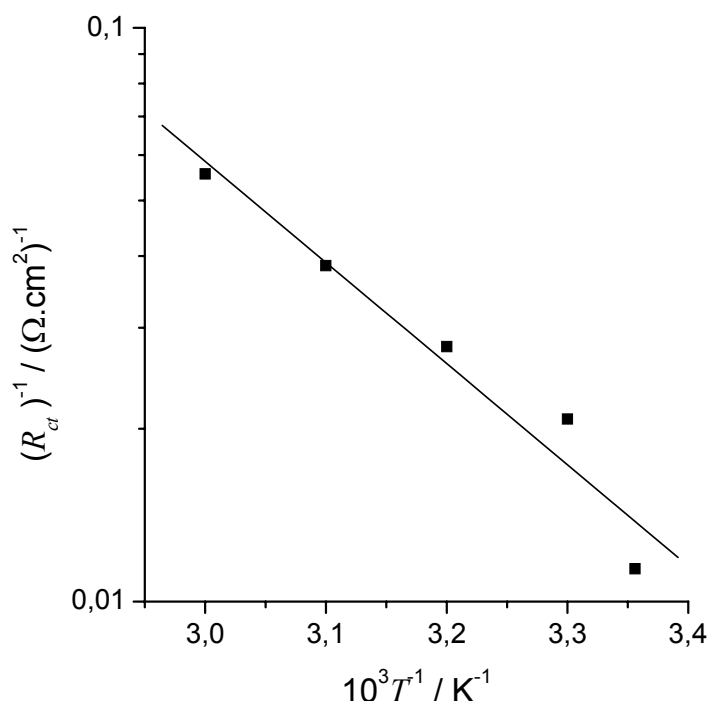


Fig. 5 – Plot of  $\log(R_{ct})_E^{-1} - T^{-1}$ , for the HER at 18Cr-10Ni stainless steel electrode in artificial seawater taken at constant potential of  $-1.28$  V vs. SCE.

## DISCUSSION

### 1. Temperature effect on the transfer coefficient

The Tafel slope parameter  $b$  is conventionally written as  $b = RT/\alpha F$ , where  $\alpha$  is the transfer coefficient and is generally considered to have a constant value of 0.5. The experimental values of  $\alpha$  show a temperature dependence (Table 2), confirming the form for  $b$  suggested by Conway<sup>6</sup> for the HER at solid state electrodes; i.e.,  $b = RT/(\alpha_H + \alpha_S T)$ . In this case,  $\alpha_H$  is the

temperature-independent ‘enthalpic’ component corresponding to the conventional behaviour and  $\alpha_S$  is the ‘entropic’ component, which gives the temperature dependence of the transfer coefficient. The values obtained from the  $\alpha - T$  plot are  $\alpha_H = 0.48$ , and  $\alpha_S = 7.4 \cdot 10^{-4} \text{ K}^{-1}$ .

### 2. Dependence of $\Delta H_E^{o\#} - E$

The dependence of the electrochemical activation enthalpy for the HER on potential,  $\Delta H_E^{o\#} - E$ , is linear, in accordance with equation:

$$\Delta H_E^{o\#} = 94.2 + 46.55E \quad (1)$$

According to theory<sup>6</sup> the line slope ( $46.55 \text{ kJ}\cdot\text{V}^{-1}\cdot\text{mol}^{-1}$  or  $46.55\cdot 10^3 \text{ C}\cdot\text{mol}^{-1}$ ) is equal to  $-\alpha_{\text{H}}F$ . The temperature independent part of the transfer coefficient for the HER calculated from the line slope of the  $\Delta H_E^{o\#} - E$  is  $\alpha_{\text{H}} \cong 0.47$ , and is close to the value obtained from the temperature dependence of the charge transfer coefficient.

The potential independent part of the electrochemical activation energy (*i.e.*, the part of the activation energy independent of potential for the HER)<sup>2, 7</sup> can be obtained from extrapolation of the straight line with slope  $\alpha_{\text{H}}F$  to  $E = 0 \text{ V}$ . In this case,  $\Delta H_E^{o\#}(E = 0) = 94.2 \text{ kJ mol}^{-1}$ . As shown by Krstajić *et al.*<sup>2</sup> this parameter can be used to examine reaction electrocatalysis when it is evaluated for various electrode materials in the same solution.

### 3. Dependence of $\log i_E(1/T = 0) - E$

Dependence of the electrochemical pre-exponential factor on potential is linear too, in accordance with equation:

$$\log i_E(1/T = 0) = 7.32 + 3.16E \quad (2)$$

According to theory<sup>6</sup> the line slope of  $3.16 \text{ V}^{-1}$  is equal to  $-(\alpha_{\text{S}}F)/R$ , where  $\alpha_{\text{S}}$  is the temperature dependent part of the charge transfer coefficient for the HER. The calculated value of  $\alpha_{\text{S}}$  is  $-2.7 \times 10^{-4} \text{ K}^{-1}$ , which is reasonably close to the value of  $-7.4 \times 10^{-4} \text{ K}^{-1}$ , obtained from the temperature dependence of the charge transfer coefficient for the HER.

Through the extrapolation of the  $\log i_E(1/T = 0) - E$  line with the ordinate at  $E = 0$ , part of the pre-exponential factor independent of potential is obtained, *i.e.*  $\log i_{E=0}(1/T = 0) = 7.32$ . This intercept at the ordinate axis is theoretically related to the entropy of activation of the HER.<sup>2, 7</sup>

### 4. The HER as activationless process

The Tafel lines (Fig.1) are not parallel—they tend to cross at some potential  $E^*$  (or overpotential,  $\eta^*$ ) such 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.<sup>8</sup> 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 from the intercept of the linear  $\Delta H_E^{o\#} - E$  dependence with the abscissa axis (*i.e.*,  $\Delta H_E^{o\#} = 0$ ). According to equation (1), the value of the final electrode potential of the enthalpy is equal to  $-2.02 \text{ V vs. SCE}$ , *i.e.*, the potential at which the HER rate on the 18Cr-10Ni stainless steel electrode in artificial seawater must be independent of the potential.

Another boundary property of the HER, the ultimate entropy potential<sup>2</sup>,  $E_{S,u}$ , can be found from the linear dependence  $\log i_E(1/T = 0) - E$  (equation 2) for the condition where  $\log i_E(1/T = 0) = 0$ . The value of the ultimate entropy potential is  $E_{S,u} = -2.316 \text{ V vs. SCE}$ .

According to Conway,<sup>6</sup> an electrode reaction can be considered to be a process without an activation barrier when both conditions  $E < E_{H,u}$  and  $E < E_{S,u}$  are satisfied. Based on the results in this paper, the HER on the 18CR-10Ni stainless steel electrode in artificial seawater is an activationless process at  $E < -2.316 \text{ V vs. SCE}$ .

## CONCLUSIONS

The hydrogen evolution reaction at an 18Cr-10Ni stainless steel electrode in artificial seawater is charge transfer controlled: it shows Tafel behaviour and clearly semicircular Nyquist impedance diagrams. The values of the kinetic parameters – exchange current density and charge transfer coefficient – are influenced by the solution temperature. The exchange current density increases significantly with temperature, being 20 times higher at 333 K than at 295 K. The transfer coefficient is significant less 0.5 and it decreases with temperature.

The formal electrochemical activation enthalpy of the HER on 18Cr-10Ni stainless steel electrode in artificial seawater has moderate values, which decrease as the applied potential is shifted toward more negative values. Comparable values are obtained from PSV and EIS measurements. The experimentally-obtained results indicate that the HER on a 18CR-10Ni electrode in artificial seawater becomes an activationless process at  $E < -2.316 \text{ V vs. SCE}$ .

The kinetic parameters and activation energy obtained in this paper are close to those reported in

the literature for Ni electrodes in alkaline solution for the HER, which means that 18Cr-10Ni stainless steel can be used as cathode for seawater electrolysis, if the chemical scaling of the electrode surface will be solved.

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