

Kinetics of the hydrogen evolution reaction on Ni electrode in synthetic seawater – an alkaline solution

Y. Petrov^{1*}, J.-P. Schosger², F. de Bruijn³

¹ *Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Science, 10 Acad. G. Bonchev Blvd., 1113 Sofia, Bulgaria*

² *Institute for Energy, Joint Research Center, Westerduinweg 3, 1755 LE Petten, the Netherlands*

³ *Energy and Sustainability Research Institute Groningen, University of Groningen, Nijenborgh 4, 9747 AE Groningen, the Netherlands*

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The electrolysis is a technology for production of hydrogen from renewable sources. Modern commercial electrolyzers focus on hydrogen as a chemical, and not as an energy carrier. For the future large-scale production for automotive applications, electrolyzer energy efficiency and the resulting hydrogen quality and cost are important factors that need more attention. The need of ultrapure water in the novel generation of electrolyzers also increases the cost, and therefore hinders their widespread introduction. The use of seawater could prove to be an economically viable solution. The current research investigates the influence of the contaminants in seawater on the hydrogen evolution reaction on Ni electrode in the temperature range of 25–80°C. The electrochemical kinetic parameters of the reaction – Tafel slope, charge transfer coefficient and exchange current density were evaluated by galvanostatic polarization and electrochemical impedance spectroscopy. Long-term stability test results are also described. All results were compared with the results, obtained in KOH prepared with ultrapure water.

Keywords: seawater electrolysis, hydrogen evolution reaction, kinetic parameters, rate constants, electrochemical impedance spectroscopy

INTRODUCTION

The present energy system, based on the conversion of fossil fuels, is not sustainable and poses environmental hazards. Based on its unique characteristics (highest heat of combustion from all fuels – $120,9 \times 10^6$ J/kg) [1], hydrogen is accredited as an energy carrier with major role in the future energy system [2–4]. In fact, it can be produced in renewable manner either directly – using sunlight or biomass, or indirectly – using electrolysis and power, supplied from wind, solar, geothermal, and hydropower sources. It can be stored or used as a fuel in fuel cells or internal combustion engines to produce electricity when needed. Contrary to the currently used methods for hydrogen production from fossil fuels, which have carbon dioxide (CO₂) and other greenhouse gas (GHGs) emissions, the combination of electrolyzers and renewable energy sources would lead to sustainable hydrogen production.

Currently there are three different technologies for water electrolysis (WE) with hydrogen (H₂) and

oxygen (O₂) as end products. Based on the type of utilized electrolyte there are: 1- the most developed and commercially available alkaline water electrolyzers (AWE) [4]; 2 – polymer electrolyte membrane electrolyzers (PEMWE) which are still under development but small-scale units are also available on the market [5]; and 3 – solid oxide electrolyzers (SOWE), being under intensive development. The main advantages of the three systems are the comparatively high purity of the obtained end products and the absence of environmentally harmful emissions. Their disadvantages could be summarized as the high energy need for the process itself and the fact that there are strict standards for the quality of the used water - ASTM D1141 type water [6]. The latter prerequisite often calls for preliminary purification of the water, requiring additional energy consumption together with additional investments for constructing purification installations. The need for ultrapure water in the novel electrolyzer generation hinders their widespread application, and contributes to the high cost of the hydrogen.

Other technologies that are based on electrolysis and have H₂ as by-product are industrially available. The chlor-alkali electrolysis [7] uses

* To whom all correspondence should be sent:
E-mail: E-mail: yanko.petrov@gmail.com

sodium chloride (NaCl) solution as electrolyte and via various cell configuration, membrane, diaphragm and mercury cell technology, sodium hydroxide (NaOH) and chlorine (Cl₂) are obtained. In all three cases, H₂ evolves at the cathode.

As the most abundant form of water on the planet, seawater would be an attractive feed for the production of hydrogen on a large scale by water electrolysis, based on renewable energy. However, there are several problems that need to be solved if hydrogen is to be produced by seawater electrolysis. Basically they are: the development of active cathodes for hydrogen evolution reaction (HER)[8, 9]; the exploring anodes that selectively evolve O₂ instead of Cl₂ [10]; or finding an environmentally safe way to dispose back the produced chlorine.

The aim of this study is to investigate the kinetics of HER on a nickel (Ni) electrode during electrolysis of synthetic seawater – an alkaline solution. Ni was chosen as a cathode material because it is known as metal with good electrocatalytic activity and stability towards HER in alkaline and neutral media even in the seawater.

EXPERIMENTAL

The working electrode (WE) was cut from 99.9% purity Ni rod (Goodfellow Cambridge Ltd.), and had an exposed geometric area of 1 cm². Specimens were polished successively with 800 and 1200-grade emery paper, washed with carbon tetrachloride, cleaned in an ultrasonic bath for 15 minutes, and then washed thoroughly with distilled water. To remove any spontaneously formed oxides before each measurement, WEs were polarized with a cathodic current of 0.3 A.cm⁻² for 30 minutes. The counter electrode (CE) was a platinum basket with high surface area. Saturated Calomel Electrode (Radiometer Analytical XR110) was employed as a reference electrode (RE), whose potential versus the Reversible Hydrogen Electrode (RHE) at 298.15 K is 0.244 V.

One compartment, 3.5L cylindrical Pyrex glass cell, equipped with water jacket for controlling the temperature by thermostat was used for the electrochemical measurements. The WE was positioned in the center while the CE was placed around it. The RE was connected to the cell through an electrolytic bridge which had a Luggin capillary, positioned close to the WE.

The artificial seawater was prepared using chemically pure reagents and 18 MΩ.cm distilled water. The composition of the artificial seawater,

containing no heavy metals and complying with ASTM D1141, is listed in Table 1.

Table 1. Artificial seawater composition according to ASTM D1141

Chemical compounds	Concentration, g/L	Chemical compounds	Concentration, g/L
NaCl	24.53	NaHCO ₃	0.201
MgCl ₂ .6H ₂ O	11.103	KBr	0.101
Na ₂ SO ₄ .10H ₂ O	9.278	H ₃ BO ₃	0.027
CaCl ₂ .2H ₂ O	1.539	SrCl ₂ .6H ₂ O	0.042
KCl	0.695	NaF	0.003

The electrochemical measurements were performed using SI 1287 Electrochemical Interface (Solartron), coupled with SI 1255 HF Frequency Response Analyzer (Solartron). The galvanostatic polarization curves ranging from 0.3 A.cm⁻² to 5 × 10⁻⁵ A.cm⁻² (2 minutes per point) were recorded until reproducible results were obtained. The electrode potentials were corrected for iR_s drop (ohmic drop), determined by Electrochemical Impedance Spectroscopy (EIS). In the EIS measurements the amplitude of the ac signal was 10 mV. A frequency range from 50 kHz to 0.1 Hz was covered with 10 points per decade. The real and imaginary components of the complex plane plots were analyzed using a complex nonlinear least-squares fitting (CNLS) program Zview 3.1 (Scribner Associates, Inc.) by which the experimental parameters of an electrical equivalent circuit were determined.

RESULTS AND DISCUSSION

Fig.1 shows the experimental iR_s corrected Tafel polarization plots of Ni electrode in artificial seawater at four temperatures under study. By extrapolation of Tafel lines to the HER equilibrium

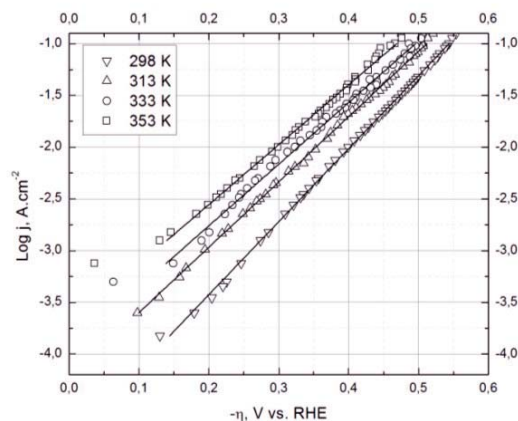


Fig. 1. iR corrected galvanostatic Tafel curves of seawater at four temperatures.

potential, the exchange current density – j_0 , is calculated, and from Tafel slope – b , the value of the charge transfer coefficient – α is obtained.

The values of the Tafel slope are higher than the theoretically calculated according to the relation – $b = 2.3RT/\alpha F$, assuming $\alpha = 0.5$. The charge transfer coefficient is ca. $\sim 0.40 \pm 0.02$ while for KOH prepared with pure water it is about 0.47 ± 0.02 , depending on the temperature. The results are summarized in Table 2. Large deviation from the theoretically calculated values of the Tafel slope are also reported in the literature for HER on various electrode materials in alkaline solution [11, 12].

Table 2. Apparent (per unit geometric area) kinetic parameters for HER in artificial seawater + 1 mol.dm⁻³ KOH at four temperatures (* - values obtained in the case of pure water + 1 mol.dm⁻³ KOH)

T, K	b , V.dec ⁻¹	j_0 , A.cm ⁻²	α	$-\eta_{100}$	$b_{theor.}$, V.dec ⁻¹
298	0,142	$1,44 \times 10^{-5}$	0,42	0,544	0,118
313	0,158	$5,84 \times 10^{-5}$	0,38	0,512	0,124
333	0,167	$11,11 \times 10^{-5}$	0,39	0,495	0,132
353	0,172	$18,70 \times 10^{-5}$	0,41	0,486	0,140
298*	0,119	$0,92 \times 10^{-5}$	0,49	0,484	0,118
313*	0,132	$4,17 \times 10^{-5}$	0,47	0,452	0,124
333*	0,143	$8,05 \times 10^{-5}$	0,46	0,441	0,132
353*	0,154	$31,92 \times 10^{-5}$	0,46	0,382	0,140

A comparison of the polarization performance of Ni electrode in pure and synthetic seawater towards HER is presented in Fig 2. On one hand, the calculated exchange current densities, obtained for seawater, are higher compared to the ones in the case of pure water except at 353 K. It should be noticed that the exchange current density is a measure of a reaction rate at the reversible potential, i.e. where the net current densities are zero. However, in reality it is possible that a reaction, having high value of j_0 , shows a lower activity at current densities which are comparable to the ones, achieved in the industrial practice. On the other hand, the registered overpotential at a constant current density of 100 mA.cm⁻² is higher in the case of seawater, indicating lower electrocatalytic activity for HER. This could be only due to the presence of contaminants in the electrolyte, because all the other experimental conditions are the same as in the case of the pure water.

The experimental electrochemical impedance spectra (EIS) of Ni electrode in artificial seawater at four constant potentials, taken from the Tafel region are presented as complex-plane (Nyquist) plot on Fig. 3.

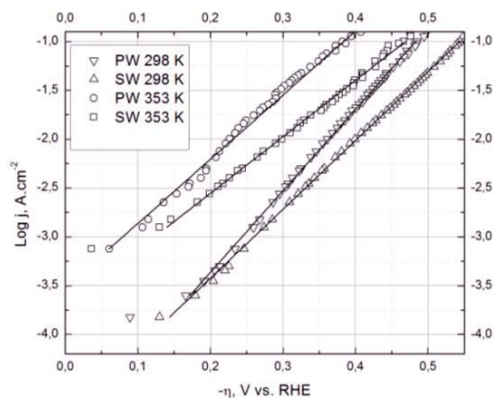


Fig. 2. iR corrected galvanostatic Tafel curves of pure water and seawater at 298K and 353K.

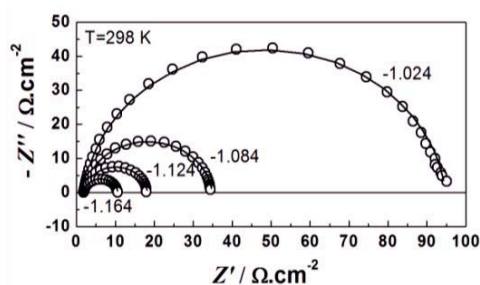


Fig. 3. Complex – plane plot of Ni electrode in artificial seawater – alkaline solution at constant temperature of 298 K and potentials -1,024;-1,084;-1,124;-1,164 V vs. RHE.

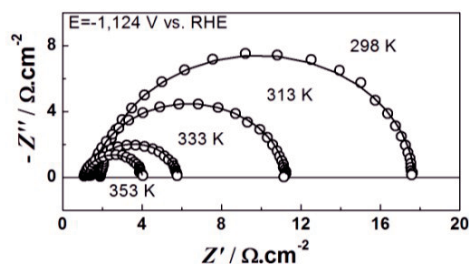


Fig. 4. Complex – plane plot of Ni electrode in artificial seawater – alkaline solution at constant potential of -1.124 V vs. RHE and four different temperatures.

One depressed capacitive loop is observed at all potentials under investigation. To analyze the experimental EIS data 1CPE equivalent circuit was used. It consists of a solution resistance R_s in serial connection with a constant phase element – CPE, which is in parallel connection with the charge transfer resistance R_{ct} . The CPE is used instead of a pure capacitor and it accounts for the inhomogeneities of the electrode surface. The double layer capacitance (C_{dl}) can be calculated according to the relation [13, 14]:

$$C_{dl} = [T(R_s^{-1} + R_{ct}^{-1})^{-(1-a)}]^{1/a} \quad (1)$$

The charge transfer resistance is related to the kinetics of the HER. Fig. 3 confirms the charge transfer controlled kinetics and shows as expected a decrease of R_{ct} with increasing cathodic polarization.

Fig. 4 shows the complex-plane plot of the system at constant potential and different temperatures. As expected, a decrease of R_{ct} values with increasing temperature is observed which confirms that the HER proceeds faster at elevated temperatures.

Table 3. Values of the equivalent circuit elements obtained with the 1-CPE model on Ni in artificial seawater + 1 mol.dm⁻³ KOH at T=298 K and five potentials (* - values obtained in the case of pure water + 1 mol.dm⁻³ KOH).

E, V vs. RHE	R_s (Ω .cm ⁻²)	T, (F.s ⁻¹ .cm ⁻²) $\times 10^{-4}$	a	R_{ct} (Ω .cm ⁻²)	C_{dl} (F.cm ⁻²) $\times 10^{-4}$
-0,984	1,88	1,51	0,93	180,24	0,818
-1,024	1,92	1,46	0,93	95,02	0,789
-1,084	1,91	1,30	0,94	32,52	0,761
-1,124	1,91	1,19	0,96	15,97	0,832
-1,164	1,89	1,06	0,97	8,38	0,809
-0,984*	1,87	10,08	0,87	211,38	3,95
-1,024*	1,94	5,91	0,91	73,13	3,02
-1,084*	1,94	3,73	0,95	21,55	2,53
-1,124*	1,96	3,43	0,96	11,03	2,51
-1,164*	1,97	3,70	0,95	6,27	2,49

Table 3 summarizes the values of the equivalent circuit elements, obtained by non-linear least squares (NLS) fitting. Values for the case of Ni in pure water are also listed for comparison. As it can be seen R_{ct} values in case of seawater are higher at more negative potentials where high current densities of practical use are reached, which is in good agreement with the results, obtained from the galvanostatic d.c. measurements. The lower values of the double layer capacitance, measured for seawater, and compared to pure water, are assumed to result from the fact that part of the electrochemically active surface is covered by adsorbed species from the electrolyte solution which lowered the available electrode surface for the HER.

Since Tafel analysis clearly indicated that the HER kinetics within the investigated potential region is charge transfer controlled, it was assumed that the η -log(R_{ct})⁻¹ relationship, presented in Fig. 5, will follow a linear trend, and will have a slope identical to the Tafel slope.

The obtained slopes, b_{ac} were found to be in accordance with those, derived from Tafel analysis of galvanostatic polarization curves.

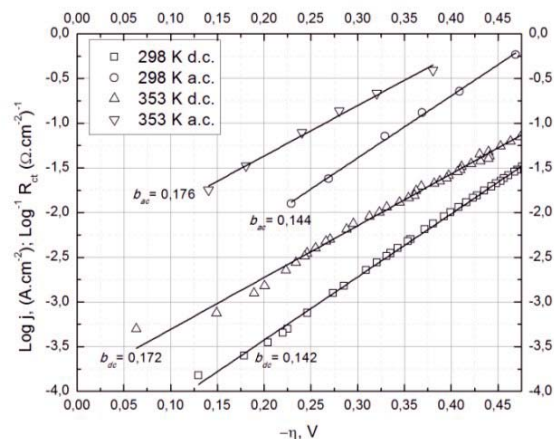
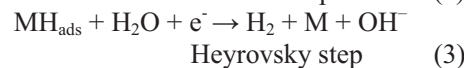
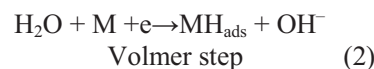


Fig. 5. Comparison of log j vs. η and obtained Tafel slopes by d.c. polarization and a.c. impedance method for seawater at 298 and 353 K.

Generally, it is accepted that in alkaline solutions the HER proceeds through three steps [15–18]:



Consecutive combinations of Volmer-Tafel and Volmer-Heyrovsky steps, in which one of them is the rate-determining step (RDS), have been proposed for the HER mechanism on different cathodic materials [16, 19–21].

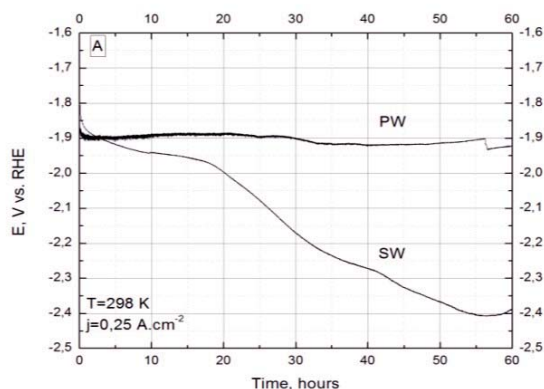
As discussed in details by Krstajic et al. [19], if we assume that the experimentally recorded current density is determined by the rate of Heyrovsky step in the potential region $E < -1.2$ V vs. RHE, then the relation will hold:

$$V_h = k_h \theta \exp(-\alpha FE/RT) = i_{ss}/2F \quad (5)$$

where V_h is the rate of the Heyrovsky step, k_h [mol.cm⁻².s⁻¹] is the chemical rate constant for the rate controlling Heyrovsky step. Then, using the current density in the experimentally obtained potential region between 1.2 and 1.3 V vs. RHE and the transfer coefficient i. e. 0.42 at 298K, the average value of $k_h = 2.42 \times 10^{-12}$ was calculated, assuming that the surface coverage by adsorbed hydrogen (θ) is ~1.

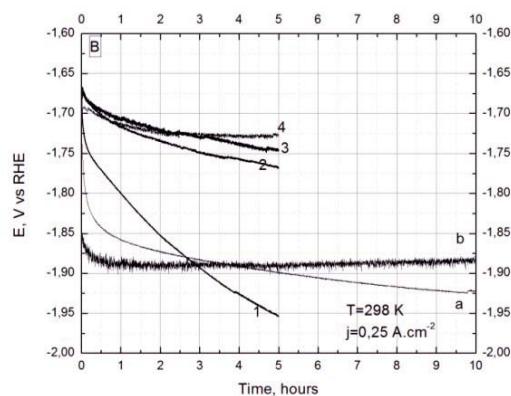
As shown, the experimentally calculated values of the Tafel slope by d.c. and a.c. techniques are higher than the theoretically expected if a proton discharge is assumed to be the RDS and $\alpha=0.5$. If the Volmer step is fast and the Heyrovsky step is slow, the surface coverage θ will approach unity and the Tafel slope will increase. Thus, the most likely mechanism for the HER under the present

conditions would be the Volmer-Heyrovsky



(a)

pathway in which the second step is the RDS.



(b)

Fig. 6 Stability test: A – 60 h at current density $0,25 \text{ A.cm}^{-2}$ at 298 K; B – comparison of potential dependence after reversing the current for 10 min. – a and b are the first 10 h taken from A

Galvanostatic d.c. and a.c. impedance measurements could account only for short-term performance of the investigated system. From a practical point of view the long-term behavior is as important as its kinetics properties. For this reason a stability test at a constant current density of 0.25 A.cm^{-2} within 60 hours was performed. As shown in Fig. 6A, the potential of the Ni electrode in artificial seawater increased with time and after 60 hours reached a value of approximately $\sim -2.4 \text{ V}$ vs. RHE at 298K. In the case of pure water the potential of the electrode also varied but in a very narrow range at around $\sim -1.9 \text{ V}$ vs. RHE. Again, it is assumed that the increase of the electrode potential in synthetic seawater is due to the poisoning effect of the impurities towards the electrochemically active surface for the HER. It is known that poisons could be adsorbed irreversibly or reversibly [22]. In the latter case it is believed that they could be removed by oxidation reaction and in this way the electrode surface could be cleaned. To verify if this effect is applicable in the case of Ni electrode in synthetic seawater another test was performed. Under the same conditions as in the stability test after 5 hours cathodic polarization, the current was reversed for 10 minutes in the positive direction. This procedure was repeated 4 times and the obtained results are shown in Fig. 6B.

Obviously, switching the current to positive direction changes the surface state of the electrode. After each cycle the potential of the electrode decreased further and stayed lower even when compared with the one of pure water under the long-term test conditions. This could be explained with the fact that the part of the electrode surface, which was not poisoned, is also oxidized by

imposing it to the positive current. It is known from the literature [23] that the HER on oxide covered Ni electrode proceeds faster than on pure metallic Ni. This behavior confirms that the poisoning effect of the impurities in the electrolyte could be overcome to some extent by reversing the current in positive direction for a certain period of time.

CONCLUSIONS

It can be concluded from the experimental results that the HER on Ni electrode in artificial seawater – an alkaline solution is charge transfer controlled. The obtained exchange current density is higher except at 353K, compared to the density in the case of the pure water. The overpotential at 0.1 A.cm^{-2} is also higher while the transfer coefficient is lower and varies little with the temperature. The high values of the Tafel slope lead to the conclusion that the reaction mechanism is a consecutive combination of the Volmer step followed by the Heyrovsky step, the latter being a rate-determining step at more negative potentials. Deactivation of the electrode performance is monitored under long-term tests most probably due to the blockage of the electrochemically available surface with impurities from the bulk electrolyte. Reversing the current for a short time proved to be efficient to some extent for cleaning the surface of the electrode.

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КИНЕТИКА НА РЕАКЦИЯТА НА ОТДЕЛЯНЕ НА ВОДОРОД ВЪРХУ НИКЕЛОВ ЕЛЕКТРОД В СИНТЕТИЧНА МОРСКА ВОДА – АЛКАЛЕН РАЗТВОР

Я. Петров^{1*}, Ж.-П. Шосгр², Ф. де Бруийн³

¹Институт по електрохимия и енергийни системи, Българска академия на науките,
ул. 'Акад. Г. Бончев', бл. 10, 1113 София

²Институт по Енергия, Съвместен изследователски център, Вестердюнвех 3, 1175 ЛЕ
Петен, Нидерландия

³Изследователски институт за устойчивост и енергия, Гронингенски университет,
Нйенборг 4, 9747 АЕ Гронинген, Нидерландия

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(Резюме)

Изследвано е влиянието на замърсителите в синтетична морска вода - алкален разтвор, върху реакцията на електрохимично отделяне на водород от никелов електрод, в температурният диапазон 25-80° С. Кинетичните параметри на реакцията - Тафелов наклон, обменен ток и коефициента на пренос на заряд са изчислени въз основа на получените галваностатични поляризационни зависимости и електрохимични импедансни измервания. Проведени и анализирани са тестове за стабилност в продължение на 60 часа. Всички стойности са сравнени с резултати получени в алкален разтвор на чиста вода.