

Hydrogen evolution reaction on Ni–Al electrodes

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The hydrogen evolution reaction (h.e.r.) was studied in alkaline solutions on two types of electrodes: (i) obtained by alloying Raney nickel without or with nickel and (ii) by pressing Raney nickel and nickel powders at room temperature. The obtained electrodes are usually very active for the h.e.r. The most active electrode was obtained by pressing Raney nickel with nickel powder (50 wt %). It was characterized by a large roughness factor, $R \sim 10\,000$ and a very low overpotential at the current density of 250 mA cm^{-2} , $\eta_{250} = 56 \text{ mV}$. The mechanism of the h.e.r. was studied using a.c. impedance measurements. The high electrode activity is connected with the increase in the intrinsic activity of the porous electrode surface.

1. Introduction

Raney type alloys are among the best catalysts for the hydrogen evolution reaction (h.e.r.) [1–14]. They consist of the electrocatalytically active metal (Ni, Co) and a more active metal (Al, Zn) which can be easily leached out in alkaline solutions. This process produces electrodes characterised by a very large surface roughness. The active electrodes were prepared by the composite electrodeposition of the Raney nickel powder with nickel [4,5], plasma spraying [1,3,6,7], electrodeposition [1,2,8–11], rolling of Ni–Al alloys [1,2], interdiffusion of aluminium [1,12], sintering [13], etc. In a recent paper [13] the mechanism and kinetics of the h.e.r. were studied on Ni–Al alloys prepared from Raney nickel powder by sintering it under high temperature and pressure. The alloy formed was active but not stable enough in the industrial electrolysis conditions (30% NaOH, 70 °C). A.c. impedance studies showed that a fractal model had to be used to explain the electrode behaviour. The h.e.r. was also studied on Ni–Zn alloys prepared by electrodeposition [11,14]. The composition of the alloy could be changed easily by changing the deposition potential [11]. These electrodes were less active towards the h.e.r. than the Ni–Al electrodes. The highest activity was found for the electrodes having the lowest nickel content (28%) and, consequently, the highest surface roughness after leaching out zinc.

In further studies nickel–zinc powder electrodes were used [15]. These electrodes were prepared by pressing nickel and zinc powders under high pressure at room temperature followed by leaching zinc in the alkaline solution. Similarly to the Ni–Zn alloy electrodes the activity increased with decrease in the nickel content. The lowest limit of the nickel content was 50%, below which the electrode disintegrated during the h.e.r. The Ni–Zn powder electrodes were less active than those prepared by electrodeposition and

were characterized by higher Tafel slopes. In the case of Ni–Zn alloy and Ni–Zn powder electrodes the a.c. impedance spectra could be explained assuming an equivalent circuit containing a constant phase element (CPE) instead of the double layer capacitance.

In the present paper Ni–Al electrodes were prepared by two methods: (i) alloying Raney nickel (Ni–Al 50 wt%) without or with nickel at high temperature and (ii) pressing Raney nickel and nickel powders at room temperature. The suitability of these electrodes for the h.e.r. was studied by steady-state polarization and a.c. impedance techniques.

2. Experimental details

The Ni–Al alloys were prepared by alloying Raney nickel (Aldrich) and nickel (Anachemia) powders at 1600 °C for one hour under an argon atmosphere in an alumina crucible of the desired shape. These electrodes had disc form with a surface area of 0.196 cm^2 . The Raney nickel–Ni powder electrodes were prepared by pressing the mixed powders at 6540 atm at room temperature. The geometric surface area was 0.785 cm^2 . Before the electrochemical studies the electrodes were leached in 30% NaOH at 70 °C for 1 h for alloy electrodes and 2 h for powder electrodes. All measurements were made in 1 M NaOH (Aldrich 99.99%) solutions using deionized water (Barnstead Nanopure). All other experimental details are given elsewhere [11,13,16,17].

3. Results

3.1. Ni–Al alloys

The first electrode studied was prepared by melting pure Raney nickel powder. The Tafel curve registered in 1 M NaOH at 25 °C is shown in Fig. 1 and the results obtained are shown in Table 1. These results are very similar to those obtained on the electrodes

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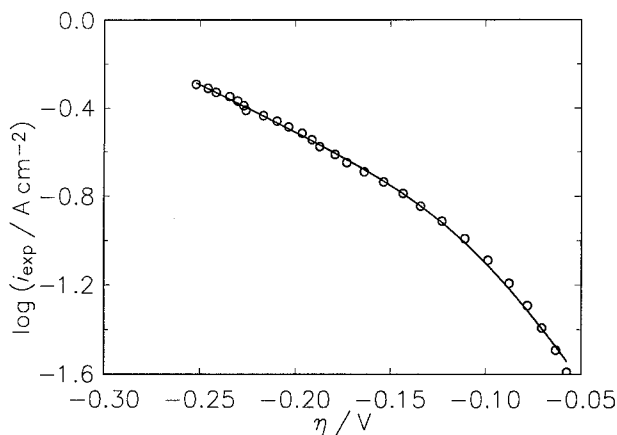


Fig. 1. Tafel curve registered on Raney nickel alloy electrode (50% Ni) in 1 M NaOH at 25°C. (O) Experimental; (—) approximated.

prepared by sintering Raney nickel powder under high pressure (1000 atm) at 1400 °C [13]. The electrode was stable in 1 M NaOH but it was slightly less stable in the industrial electrolysis conditions (30% NaOH, 70 °C).

The a.c. impedance measurements showed one deformed semicircle on the complex plane, Fig. 2, which could be described by the fractal model, similarly to the results obtained earlier [13]. In this model the electrode impedance is given as:

$$\hat{Z}_t = R_s + \frac{1}{b} \left(\frac{1}{A + j\omega C_{dl}} \right)^\Phi \quad (1)$$

where R_s is the solution resistance, b is a product of the electrolytic conductivity and a geometrical factor, $A = 1/R_{ct}$ is the inverse of the charge transfer resistance, ω is the angular frequency, C_{dl} is the double layer capacitance and Φ is a dimensionless constant between 0 and 1. As has been shown earlier [13] the determination of the parameters A , C_{dl} and rate constants, k_i , is impossible because the parameter b is not known. The only experimentally determinable parameters are those multiplied by $b^{1/\Phi}$. The dependence of the parameter A on overpotential is presented in Fig. 3.

The a.c. impedance measurements gave $C_{dl,exp} =$

Table 1. Results of the steady-state polarization experiments for the h.e.r. at the pressed Raney nickel–nickel powder electrodes obtained after leaching out aluminium

Raney Ni /wt%	Temp. /°C	i_0 /mA cm ⁻²	b /mV dec ⁻¹	η_{250} /mV	r^2
Alloy electrodes					
100	25	37	217	174	0.995
Powder electrodes					
1 M NaOH					
50	25	14	121	156	0.993
50	70	35	62	56	0.976
70	70	31	103	100	0.990
50*	70	37	88	77	0.976
30% NaOH					
50	70	23	146	165	0.990

*After electrochemical oxidation

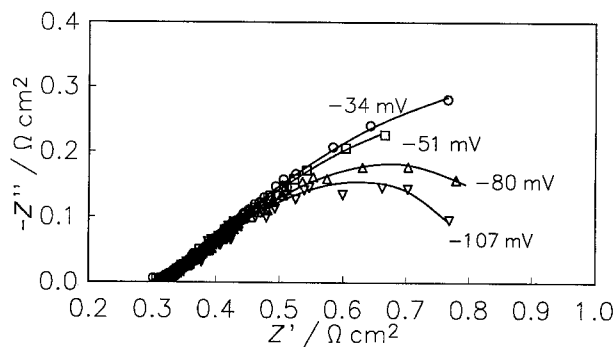


Fig. 2. Complex plane graphs obtained on Raney nickel alloy electrode in 1 M NaOH at 25°C. (O, □, △, ▽) Experimental; (—) approximated using CNLS program.

$C_{dl} b^{1/\Phi} = 10^{-12} F^{1/\Phi} \text{ cm}^{-2/\Phi} s^{(\Phi-1)/\Phi}$ and $\Phi = 0.42$ to 0.44.

On the fractal electrode the steady-state current, i_{exp} , is described by equation [18]:

$$i_{exp} = s(i)^\Phi \quad (2)$$

where i is the Tafel current and s is a constant parameter. In the case of the h.e.r. the current is calculated using the rate constants [11,13,17,20], $i = F(v_1 + v_2)$, where v_1 and v_2 are the rates of the Volmer and Heyrovsky steps, respectively. Equation 2 indicates that the Tafel slope in the linear region is $\alpha\Phi$ (α being the transfer coefficient), which for $\Phi = 0.5$, leads to doubling of the Tafel slopes [19]. In our earlier paper [13] the value of Φ in Equation 2 was assumed to be one.

The approximation of i_{exp} and A values as functions of the overpotential was carried out using a nonlinear least-squares technique [11,13,15–17]. The continuous lines in Figs 1 and 3 are those obtained by approximation.

The hydrogen evolution mechanism could be explained by assuming the Volmer–Heyrovsky mechanism, with $k_{1,exp} = k_1 b^{1/\Phi} = (2.03 \pm 0.08) \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$, $k_{-1}/k_2 = 59$ (k_{-1} and $k_2 \gg k_1$) and $s = 0.22 \pm 0.02$ for $\alpha_1 = \alpha_2 = 0.5$ and $\Phi = 0.5$ (assuming $b = 1$).

In order to improve the mechanical stability of the electrode, Raney nickel was mixed with nickel powder

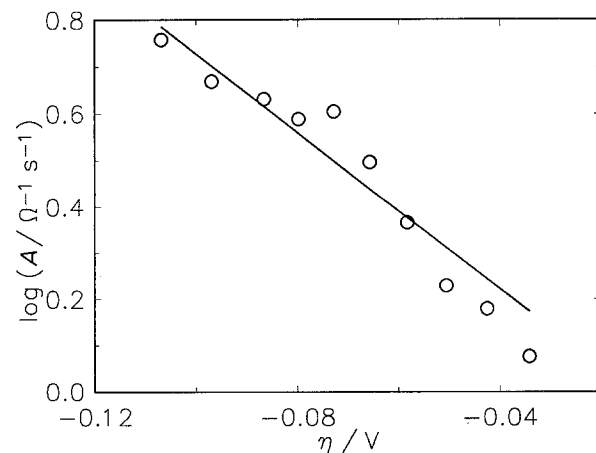


Fig. 3. Dependence of the parameter A on overpotential for the electrode in Fig. 1 (O) Experimental; (—) calculated.

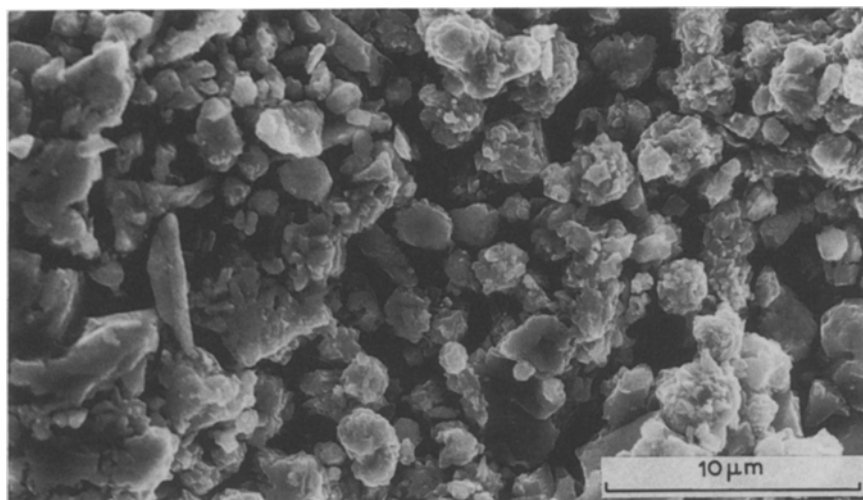


Fig. 4. SEM picture of the Raney nickel–nickel (50%) pressed powder electrode after leaching out aluminium in 30% NaOH at 70 °C for 2 h, magnification 3 500 ×.

and heated to 1600 °C. The electrode obtained from 80% of Raney nickel and 20% of nickel powder (60% Ni in the alloy) showed $\eta_{250} = 182$ mV at 25 °C (after leaching) but it was much less stable mechanically than the former one. Finally, the electrode made of 60% of Raney nickel and 40% of nickel powder (70% Ni in the alloy, atomic ratio $\sim 1 : 1$) showed a very low activity towards h.e.r with $\eta_{250} = 507$ mV. It showed resistance to the leaching procedure, probably because of the formation of the NiAl phase [1].

3.2. Raney nickel–nickel powder electrodes

3.2.1. Tafel curves. In further studies the electrodes obtained by pressing Raney nickel and nickel powders were used to produce the electrodes. The electrodes containing 50% of Raney nickel had good mechanical and electrochemical stability.

Figure 4 presents a SEM picture of the electrode containing 50% of Raney nickel powder after being leached in 30% NaOH at 70 °C for 2 h. Many deep pores are visible on the electrode surface.

The electrodes are very active towards the h.e.r. Before measurements the electrodes were polarized at a constant current for ~ 20 h until subsequent Tafel plots were identical. An example of a Tafel plot obtained at 25 °C is shown in Fig. 5 and Table 1 presents results of the steady-state polarization experiments.

The electrode containing 50% of Raney nickel is stable and very active, η_{250} is only 56 mV at 70 °C in 1 M NaOH. Its activity at 25 °C is lower. The Tafel parameters were determined in a narrow potential range using all experimental points and the slopes did not reach their limiting values expected at more negative potentials. The standard deviations and the squares of the correlation coefficients are also presented in Table 1.

In the earlier studies it was found that an electrochemical oxidation of the nickel [16] and composite coated Raney nickel electrodes [17] improves the electrode activity. However, in the present case after the electrochemical oxidation by sweeping the electrode

potential to 1 V vs. equilibrium potential, the electrode activity decreased (increase in b and η_{250}).

In 30% NaOH at 70 °C the electrode activity is lower (Table 1), similar results were also found for other electrodes [20,21]; the Tafel slope is larger (146 mV dec $^{-1}$), the exchange current density lower and $\eta_{250} = 165$ mV. It should be stressed that the electrode is mechanically and electrochemically stable for one week of electrolysis at a current density of 1.25 A cm $^{-2}$ in 30% NaOH at 70 °C.

The electrodes containing more Raney nickel (70%, Table 1) are less stable mechanically and the electrodes containing less Raney nickel are less active.

3.2.2. A.c. impedance. The a.c. impedance measurements showed the presence of one semicircle on the complex plane. These results could be explained assuming a simple model consisting of the solution resistance, R_s , in series with the parallel connection of the CPE and the faradaic impedance [11,16,17,20], represented in this case by $Z_f = A = 1/R_{ct}$. The impedance of the CPE is given as [22]:

$$Z_{CPE} = 1/T(j\omega)^\Phi \quad (3)$$

where T is connected with the average double layer capacity, C_{dl} [11,15,16,22] and Φ is a constant between 0 and 1 corresponding to the rotation angle of

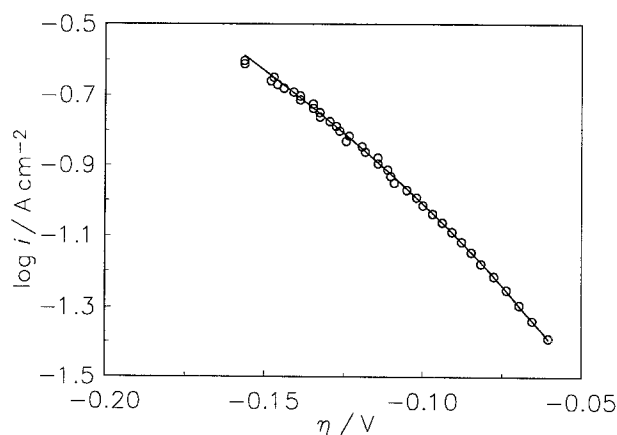


Fig. 5. Tafel curves obtained on Raney nickel–nickel (50%) powder electrode in 1 M NaOH at 25 °C. (○) Experimental; (—) calculated using data from Table 2.

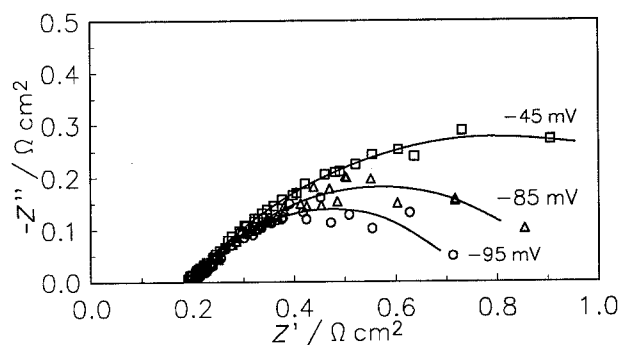


Fig. 6. Complex plane plots obtained on Raney nickel-nickel (50%) powder electrode in 1 M NaOH at 25°C. (□, Δ, ○) experimental; (—) approximated using CNLS program.

90°(1 - φ). Examples of the complex plane impedance graphs obtained in 1 M NaOH at 70°C are shown in Fig. 6. The CPE rotation parameter φ is displayed in Fig. 7. It is practically independent of the overpotential and has low values between 0.55 and 0.62.

It is possible to estimate C_{dl} from T values [11,15,17,20–22]. The results are presented in Fig. 8. The double layer capacity at 25°C does not depend on the electrode potential and has a very large value of $\sim 0.08 \text{ F cm}^{-2}$. At 70°C the capacity decreases with the increase in the hydrogen overpotential. Assuming the double layer capacity of a smooth metal surface as $20 \mu\text{F cm}^{-2}$ the surface roughness, R , of ~ 4000 at 25°C and $\sim 10^5$ at 70°C can be obtained.

The A values determined from the impedance measurements are shown in Fig. 9. There is a linear dependence of $\log A$ against η with the slope of 158 mV dec^{-1} .

The Tafel currents and A values were approximated assuming the Volmer–Heyrovsky reaction mechanism, similarly to our earlier studies [11,13,15–17,20,21]. It was also assumed that the transfer coefficients of these two reactions are equal to 0.5 [16,17,20,21]. Only at 25°C it was necessary to use the transfer coefficients as adjustable parameters. In this case the transfer coefficient found for the Volmer step was 0.5, however that for the Heyrovsky step was much lower and equal to

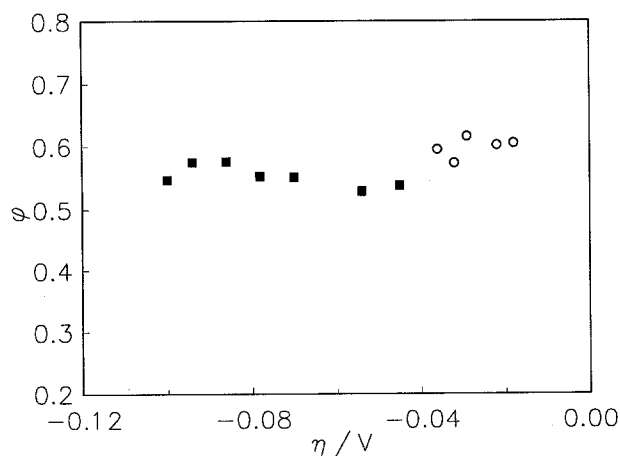


Fig. 7. Constant phase angle as a function of the overpotential for Raney nickel-nickel (50%) powder electrode in 1 M NaOH at 25°C (■) and 70°C (○).

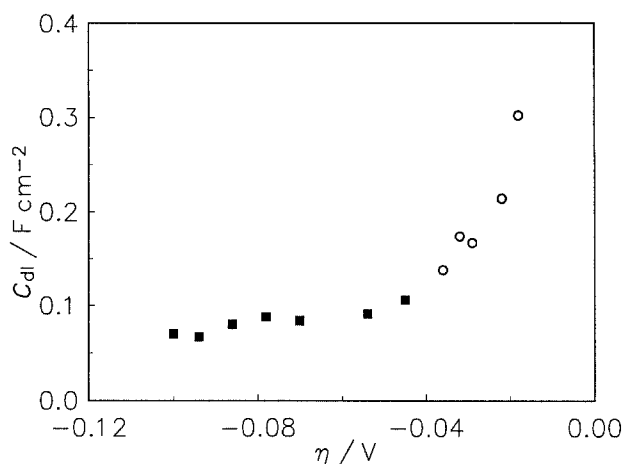


Fig. 8. Double layer capacities of the Raney nickel-nickel (50%) powder electrode in 1 M NaOH at 25°C (■) and 70°C (○).

0.23. The determined rate constants are shown in Table 2. From the comparison of the results obtained at 25 and 70°C it is evident that the kinetics of the h.e.r. are much faster at higher temperature.

The electrochemical oxidation changes the a.c. behaviour of the electrode, with the formation of two semicircles in the complex plane, similarly to the results obtained on composite coated Raney nickel electrode [17,20]. However, the second semicircle appearing at low frequencies is distorted and difficult to approximate. Therefore, only the first semicircle was used in the approximations. The kinetic parameters obtained are displayed in Table 2. The rate constant k_1 is almost three times lower than that obtained on non-oxidized electrodes.

It is also interesting to note that the roughness factor depends on the temperature and electrode preparation (Table 3). It increases with the increase in temperature and decreases after the electrochemical oxidation.

Table 3 includes values of the exchange current density and the smallest rate constant (k_1), recalculated on the real electrode surface area. These values are higher than those found for a polycrystalline nickel, $i_0 = 1.8 \mu\text{A cm}^{-2}$ and $k_1 = 4 \times 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}$

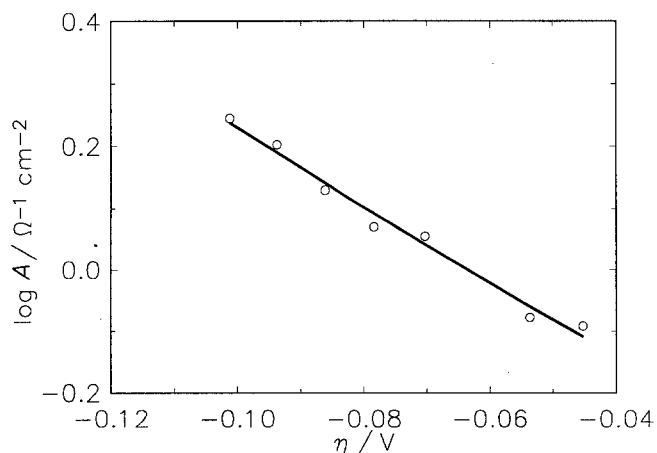


Fig. 9. Dependence of the parameter A on overpotential for the Raney nickel-nickel (50%) powder electrode at 25°C. (○) Experimental; (—) calculated using data from Table 2.

Table 2. Kinetic parameters for the h.e.r. on Raney nickel–nickel (50%) powder electrode in 1 M NaOH

Conditions	Temp. /°C	$k_1 \times 10^6$ /mol cm ⁻² s ⁻¹	$k_{-1} \times 10^6$ /mol cm ⁻² s ⁻¹	$k_2 \times 10^6$ /mol cm ⁻² s ⁻¹	α_1	α_2
No oxidation	25	0.107 ± 0.005	1.7 ± 0.5	0.76 ± 0.17	0.52 ± 0.02	0.23 ± 0.04
	70	1.33 ± 0.07	9.4 ± 1.7	1.8 ± 0.3	0.5*	0.5*
Electrochemical oxidation	70	0.46 ± 0.01	0.22 ± 0.01	5.2 ± 0.3	0.5*	0.5*

*Assumed

[16]. It should be stressed that the electrode surface is not structurally homogeneous but consists of a porous nickel from the leached Raney nickel and a fractal nickel powder.

4. Discussion

Two electrode materials based on Raney nickel were studied for the h.e.r. in alkaline solutions. The electrodes obtained by alloying Raney nickel were characterized by high activity towards the h.e.r. (Table 1). The electrode prepared by alloying pure Raney nickel was stable in 1 M NaOH, but showed lower stability in 30% NaOH at 70 °C. Its activity is similar to that of electrodes prepared by sintering Raney nickel at high pressure and temperature. However, the electrode prepared using 80% Raney nickel and 20% nickel (60% nickel in alloy) disintegrated during the h.e.r. and the electrode containing 60% Raney nickel (70% Ni in the alloy) was not leachable, probably because of the formation of the NiAl phase. The a.c. impedance studies have shown that the fractal model should be used to explain its behavior, similarly to the Raney nickel sintered alloy electrode [13]. The mechanistic studies demonstrated that the h.e.r. proceeds by the Volmer–Heyrovsky mechanism, but the direct determination of the parameters is impossible because the parameter b , Equation 1, is not known. It is interesting to note that the Φ parameter takes values slightly lower than 0.5, the lowest value predicted theoretically [24]. This result is similar to that found earlier [13] for the Raney nickel sintered electrodes.

The electrodes prepared by pressing of Raney nickel and nickel powders are very active. The best activity and stability is obtained with the electrode containing 50% Raney nickel. Its activity is larger than that of the electrocodeposited [17,20] or sintered [16] Raney nickel, polycrystalline rhodium [25] and comparable with Ni–Rh polymer bonded electrodes [21].

The electrode obtained after leaching is very porous

Table 3. Roughness factors (R) and kinetic parameters recalculated on the real electrode surface for the Raney nickel–nickel pressed powder electrodes in 1 M NaOH

Conditions	Temp. /°C	R	i_0/R /μA cm ⁻²	k_1/R /mol cm ⁻² s ⁻¹
No oxidation	25	4000	3.5	2.7×10^{-11}
	70	10000	3.5	1.3×10^{-10}
Electrochemical oxidation	70	3500	10	1.3×10^{-10}

(see Fig. 2) and is characterized by a very large surface area. In fact, the surface roughness, estimated by comparison of the electrode capacity with that of the pure nickel, reaches a value of 10 000 in 1 M NaOH at 70 °C (Table 3). It is interesting to note that the roughness factor depends on the temperature and electrode preparation. The increase in R with temperature may be connected with the decrease in the solution viscosity and a greater accessibility of the smaller or deeper pores to the h.e.r. The surface roughness found here may be compared with values of 8 000 and 2 800 found for electrocodeposited Raney nickel powder [4,17], a value of 20 000 found for Raney nickel sintered alloy [13], 12 000 for an amorphous nickel boride and 50 000 found for amorphous nickel boride–nickel (90%–10%) pressed powder electrodes [23].

The electrochemical oxidation caused a decrease in the surface roughness (R drops to 3 500) which may be explained by the structural changes on the electrode surface, or by the decrease in the electrode specific capacity because of nickel hydroxide formation (a value of 20 μF cm⁻² was assumed in the calculation of the surface roughness).

It is interesting to note that for the pressed electrodes the electrical model containing CPE instead of the double layer capacity works the best. This result is in agreement with those obtained on nickel boride–nickel pressed powders [23], electrocodeposited Raney nickel [17,20], nickel–zinc [11,15] and other [21] electrodes.

The analysis of the a.c. impedance and Tafel curves showed that the h.e.r. proceeds through the Volmer–Heyrovsky mechanism with transfer coefficients of 0.5 except the h.e.r. at 25 °C, where $\alpha_2 = 0.23$ was found from the nonlinear least squares fit. The rate constants increase with the increase in temperature; k_1 increases about 13 times when the temperature increases from 25 to 70 °C. The electrochemical oxidation does not improve the overall electrode activity, in contrast to nickel [16] or electrocodeposited Raney nickel [17,20] electrodes.

The analysis of the kinetic parameters recalculated for the real surface area using the estimated surface roughness factors indicate that the rate of the slowest step (Volmer) is much larger than that found for the polycrystalline nickel electrode [16]. It should be kept in mind that the electrode is not structurally homogeneous and contains fractal nickel and porous nickel obtained by leaching the Raney nickel. Since the double layer capacity measurements yield average surface roughness, the activity of the Raney nickel

catalyst must be much higher and it is evident that there is a catalytic effect of the electrode surface. The activity of the pressed nickel powder is much lower than that of the Raney nickel, $b = 180 \text{ mV}$, $i_0 = 1.1 \text{ mA cm}^{-2}$, $\eta_{250} = 426 \text{ mV}$ [21].

Further studies of the long term stability of these electrodes are being carried out.

Acknowledgements

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