JOURNAL OF APPLIED ELECTROCHEMISTRY **26** (1996) 397–402

A study of RuO_2 as an electrocatalyst for hydrogen evolution in alkaline solution

N. SPĂTARU*

Institute of Physical Chemistry of the Romanian Academy, Spl. Independentei 202, 77208 Bucharest, Romania

J.-G. LE HELLOCO, R. DURAND

Centre de Recherche en Electrochimie Minérale et Génie des Procédés, 38402 St Martin D'Hères, BP 75, France

Received 7 February 1995; revised 20 August 1995

The hydrogen evolution reaction (HER) on RuO_2 coated nickel electrodes was investigated by d.c. polarization studies and a.c. impedance measurements in alkaline solution. The electroactive RuO_2 coatings were prepared by thermal decomposition of a $RuCl_3$ solution at 450 °C in air. The real surface area of the cathodes was estimated from cyclic voltammetric measurements and from the double layer capacitance (evaluated by impedance measurements). A mechanism for the HER has been proposed involving two steps (Volmer and Heyrovsky reactions). The rate constants of the forward and backward reactions of these two steps have been estimated by a nonlinear fitting procedure.

1. Introduction

Although transition metal oxides have been used as electrocatalysts mainly for anodic reactions, their good electrocatalytic performance for cathodic hydrogen evolution has been also claimed [1–3]. In spite of this there are few papers in the literature dealing with kinetic aspects of the hydrogen evolution reaction (HER) at oxides [4–6]. In fact, except for Trasatti's comparative analysis of the kinetic parameters for RuO_2, IrO_2, and Co_3O_4 [7], no systematic study of hydrogen evolution on oxide cathodes in alkaline solution has been published.

The present paper reports a study of the HER in alkaline media on the RuO_2 coated nickel electrodes, both by d.c. and a.c. measurements, in order to obtain new experimental results concerning the mechanism and the kinetic parameters of the reaction. The voltammetric behaviour of supported RuO_2 electrocatalyst has been also investigated with the purpose of obtaining information about the real surface area of the cathodes.

2. Experimental details

The electroactive RuO_2 coatings were prepared by thermal decomposition of a $RuCl_3$ solution at 450 °C in air. The nickel substrate (10 mm × 10 mm × 0.5 mm plates) was sand-blasted to obtain the rough surface which ensures good adherence of the oxide layer.

The measurements were performed in a 1 M NaOH solution, deaerated with argon for 30 min prior to each experiment. The cyclic voltammograms were recorded using a PAR 273 potentiostat and a Kipp & Zonen x–y recorder. Cathodic polarization measurements were carried out by first conditioning the electrodes for 2 h with hydrogen evolution at a current density of 100 mA cm^{-2}. The potential was reduced in 10 mV steps and the current was read after 3 min at each potential. The results were corrected for the ohmic drop deduced through high-frequency a.c. measurements. The impedance measurements were carried out using a Solartron 1250 frequency response analyser and a Solartron 1186 electrochemical interface.

All the measurements were performed at a temperature of 20 °C in a glass cell with a working electrode of 2 cm^2 area and two platinum counter electrodes in a plane symmetric configuration. As reference, a $Hg/HgO,OH^-$ electrode in the same 1 M NaOH solution, linked to the main compartment via a Luggin capillary, was used.

3. Results and discussion

3.1. *Cyclic voltammetry*

Burke and Murphy [8–10] have described cyclic voltammetry as a valuable technique for determining the surface area of RuO_2 electrodes. Thus, to characterize the surface state of the RuO_2 coated nickel cathodes voltammetric curves were recorded in a potential range −0.630 and +0.320 V, so that reproducible peak-free curves were obtained.

Typical voltammograms obtained with a sweep rate of 19 mV s^{-1} are shown in Fig. 1 for a RuO_2 coated electrode (4.2 mg cm^{-2}), before (curve 1) and after (curve 2) hydrogen evolution (2 h at 100 mA cm^{-2}). The voltammograms show that the voltammetric charge (Q) is fairly large and uniformly distributed throughout the whole potential range, which allows

* To whom correspondence should be addressed.

0021-891X © 1996 Chapman & Hall

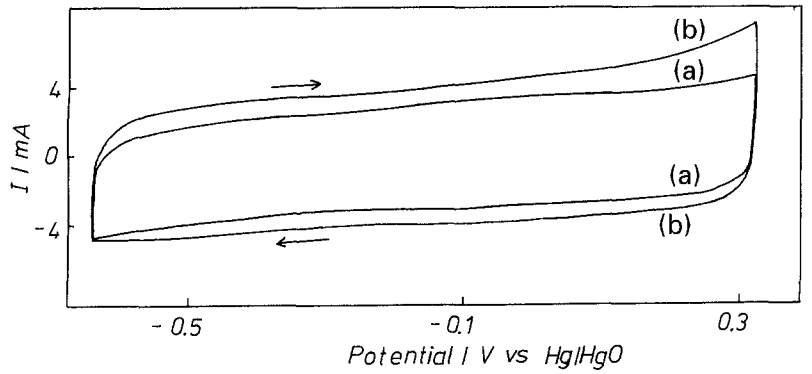

Fig. 1. Voltammograms of RuO_2 coated electrodes (4.2 mg cm^{-2}) obtained in 1 M NaOH at 20 °C and a sweep rate of 19 mV s^{-1}, (a) before and (b) after hydrogen evolution.

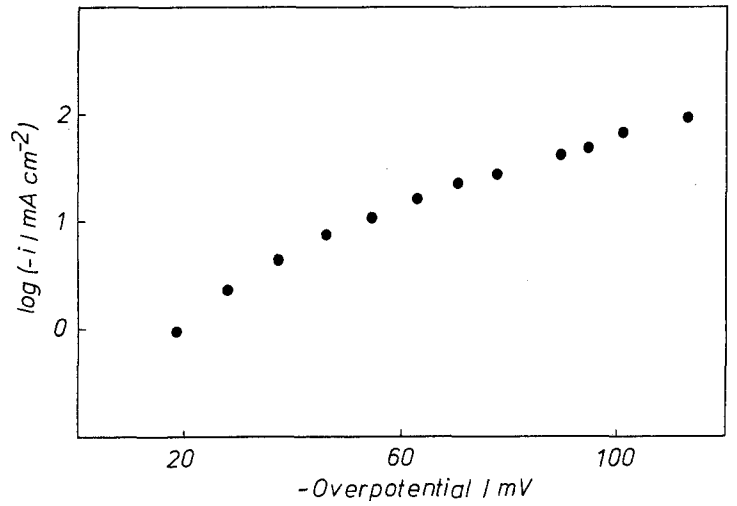

Fig. 2. Polarization curve (at 20 °C) for HER on RuO_2 coated cathodes, in 1 M NaOH.

use of Q for determining the surface area of the electrodes. It was observed that the conditioning of the cathodes results in an increase in the voltammetric charge from 68.77 mC cm^{-2} (for the fresh electrodes) to 98.37 mC cm^{-2}, although the shape of the curves does not change. This behaviour was also observed in acidic solution [11] and is probably due to an enhancement of the active area of the electrodes which is produced by the hydrogen evolution. It was previously suggested [12] that wetting is promoted by strong hydrogen discharge, which results in an increase in the available active surface of the RuO_2 coatings.

Using a value of the interfacial charge of 1.51 C m^{-2} for the RuO_2 in alkaline solution over same potential range −0.630, +0.320 V [9] a roughness factor of 651 was found (after conditioning) for the cathodes covered with 4.2 mg cm^{-2} RuO_2.

3.2. *Polarization studies*

Since the cyclic voltammetric measurements showed that the active surface area of the RuO_2 electrodes was increased by hydrogen evolution, polarization studies were carried out after holding the working electrode at a constant cathodic current density of 100 mA cm^{-2} for 2 h. This treatment resulted in reproducible polarization curves. The cathodic polarization curve of RuO_2 coated (4.2 mg cm^{-2}) nickel electrodes shown in Fig. 2 was obtained in 1 M NaOH solution saturated with hydrogen. The Tafel slope for the HER is close to 37 mV decade^{-1} in the low overpotential range, while it is close to 70 mV decade^{-1} at higher overpotential. Most of the previous studies reported a single Tafel slope for HER on RuO_2. Thus, a value of 40 mV decade^{-1} was found in alkaline solution [7, 13] while in acidic solution the Tafel slope is close to 60 mV decade^{-1} [11]. The change of the Tafel slope at higher current density was generally attributed to uncompensated ohmic drop [7, 11]. Nevertheless, a second slope of 120 mV decade^{-1} was found for Ni–RuO_2 cathodes [5]. The overpotential at a cathodic current density of 100 mA cm^{-2} and the exchange current density (estimated from the second Tafel slope) for an apparent surface area of 2 cm^2 were 115 mV and 2 mA cm^{-2}, respectively. The electrocatalytic properties of the investigated electrodes are comparable with those for smooth nickel and Raney nickel, for which the overpotential at a current density of 100 mA cm^{-2} is 210 mV and 80 mV, respectively [14]. It is to be noticed that, unlike the Raney nickel, the performances of the RuO_2 cathodes do not deteriorate with use and they have excellent tolerance to repeated short-circuitings in industrial chlor-alkali electrolysis [13]. It was also observed that their performances are not affected by Fe impurity in the catholyte [5].

Hydrogen evolution in alkaline media is generally accepted to proceed via the steps (Equations 1 to 3) noted below. The mechanism involves initial proton discharge to form an adsorbed hydrogen atom on the metal surface, MH (Volmer reaction, Equation

1) followed by the electrochemical desorption of the hydrogen (Heyrovsky reaction, Equation 2) and/or the chemical desorption by the recombination of the adsorbed H atoms (Tafel reaction, Equation 3).

$$M + H_2O + e^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MH + OH^- \quad (1)$$

$$MH + H_2O + e^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2 + M + OH^- \quad (2)$$

$$MH + MH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} H_2 + 2M \quad (3)$$

The rate constants k_i and k_{-i} (of the forward and backward reactions, respectively, for the ith step) include concentration of OH^-, H_2O and H_2 pressure and are in the same units as the reaction rates.

In the elucidation of the mechanism from the rate-determining step (r.d.s.) of a multistep reaction the Tafel slope, b, plays a prominent part. This parameter can be calculated as $b = 2.303\,RT/(\alpha F)$ in which α (the charge transfer coefficient) varies according to the r.d.s. [15]. Usually the relationships used as guidelines for interpreting kinetic parameters are based upon the limiting behaviour, that is, when the coverage by adsorbed intermediates (θ) is either zero or unity. Assuming symmetry factors $\beta = 0.5$ for both the electrochemical steps (Equations 1 and 2), the following criteria are found [15]: when the r.d.s. is Equation 1, $\alpha = 0.5$ and $b = 116\,\text{mV decade}^{-1}$, both for $\theta \to 0$ or $\theta \to 1$; when the r.d.s. is Equation 2, $\alpha = 1.5$ and $b = 39\,\text{mV decade}^{-1}$ if $\theta \to 0$, or $\alpha = 0.5$ and $b = 116\,\text{mV decade}^{-1}$ if $\theta \to 1$ and finally, if Equation 3 is the r.d.s., $\alpha = 2$ and $b = 29\,\text{mV decade}^{-1}$ if $\theta \to 0$ and $b \to \infty$ if $\theta \to 1$. A general mechanism for HER in acidic solution was previously proposed [11], suggesting that hydrogen evolution is limited by a chemical step after the primary discharge.

Here, for the investigated electrodes, the Tafel slopes and the α values are $b = 37\,\text{mV decade}^{-1}$ and $\alpha = 1.57$ in the low overpotential range and $b = 70\,\text{mV decade}^{-1}$ and $\alpha = 0.83$ at overpotentials higher than 70 mV. Thus, it may be concluded that, in the low overpotential range, the surface coverage is low ($\theta \to 0$) and the Heyrovsky step (Equation 2) must control the HER on RuO_2. This assumption is in agreement with the conclusion of Wen and Hu [16] that the rate-determining step is the desorption of hydrogen. The fact that the Tafel slope increases at higher overpotentials indicates that, in this case, it is not possible to neglect the effect of the Volmer reaction (Equation 1) on the overall HER. Nevertheless, b remains rather low (comparative with the calculated value of $116\,\text{mV decade}^{-1}$). This may be due to the fact that the second experimental Tafel slope ($70\,\text{mV decade}^{-1}$) was measured within a potential range in which the HER is controlled both by the steps (1) and (2). It is most likely that the Tafel reaction (Equation 3) does not play a significant role in the HER mechanism on RuO_2 under the investigated conditions. The same mechanism was proposed by Trasatti [7,17] with the only difference that the change of the Tafel slope at high current density was accounted for in terms of uncompensated ohmic drop.

3.3. *Impedance measurements*

Based upon the results of the polarization studies, only the first two steps (Equations 1 and 2) were assumed for the mechanism of the HER on RuO_2 in alkaline solution. The reaction rates of these two steps are related to the fractional surface coverage (θ) by

$$v_1 = k_1(1-\theta)P^{-1} - k_{-1}\theta P \quad (4)$$

$$v_2 = k_2\theta P^{-1} - k_{-2}(1-\theta)P \quad (5)$$

in which $P = \exp(\eta\beta F/RT)$, assuming the same symmetry factor β for both steps. At the steady-state conditions the surface coverage, θ, can be represented by

$$\theta = \frac{(k_1P^{-1} + k_{-2}P)}{(k_{-1} + k_{-2})P + (k_1 + k_2)P^{-1}} \quad (6)$$

It was shown [18] that for this mechanism the faradaic impedance (Z_F) can be written as

$$\frac{1}{Z_F} = A + \frac{B}{j\omega + C} \quad (7)$$

where

$$A = (\beta F^2/RT)[\{k_1(1-\theta) + k_2\theta\}P^{-1} + \{k_{-1}\theta + k_{-2}(1-\theta)\}P] \quad (8)$$

$$B = -(\beta F^3/qRT)\{(k_1 - k_2)P^{-1} + (k_{-1} - k_{-2})P\}[\{k_1(1-\theta) - k_2\theta\}P^{-1} + \{k_{-1}\theta - k_{-2}(1-\theta)\}P] \quad (9)$$

$$C = (F/q)[(k_1 + k_2)P^{-1} + (k_{-1} + k_{-2})P] \quad (10)$$

in which q stands for the maximum surface charge for $\theta = 1$. The total impedance (Z_T) can be represented by a parallel combination of the double-layer capacitance with the faradaic impedance (Z_F) and a series combination with the solution resistance (R_S). For the HER a useful equivalent circuit was suggested [19] for Z_F, containing R_∞, R_P and C_P:

$$Z_F = R_\infty + \frac{R_P}{1 + j\omega\tau_P} = R_\infty + Z_P \quad (11)$$

where $R_\infty = 1/A$, $R_P = -B/\{A(AC + B)\}$, $\tau_P = R_PC_P$, $C_P = -A^2/B$ and Z_P is an impedance which includes the time constant τ_P which characterises the time dependence of the relaxation phenomenon of the surface coverage. Therefore, the total impedance can be expressed as

$$Z_T = R_S + \frac{R_\infty}{(1 + Z_P/R_\infty)^{-1} + j\omega\tau_d} \quad (12)$$

where $\tau_d (\tau_d = C_dR_\infty)$ indicates a charge-transfer reaction through double-layer capacitance.

Since the surface of the RuO_2-coated electrodes is a nonuniform rough surface, the equivalent circuit suggested for the HER is that shown in Fig. 3, in which the double-layer capacitance is replaced by

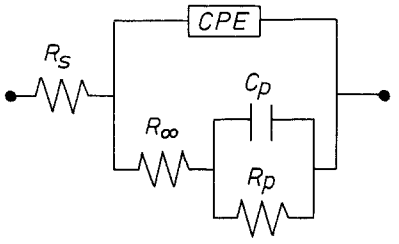

Fig. 3. Equivalent circuit for the HER on RuO_2 coated cathodes, in 1 M NaOH.

the constant phase element (CPE): this is why the term $j\omega\tau_d$ in Equation 12 becomes $(j\omega\tau_2)^{\Phi}$. The use of a CPE replacing the double layer seems to be a good approach for the study of some practical electrodes with different degrees of surface roughness, with physical nonuniformity or with a distribution of surface reaction sites [18, 20, 21].

The experimental impedance spectra were analysed using a complex nonlinear least squares (CNLS) fitting program [22] to estimate the parameters R_∞, R_P and C_P as well as the parameters of the CPE (τ_2 and Φ). Figure 4 shows the experimental and the simulated plots (calculated from CNLS fitting) for the impedance spectra of the RuO_2 coated (4.2 mg cm^{-2}) electrodes, at several values of the applied potential. A good agreement between the experimental and simulated impedance spectra is observed over a wide overpotential range. Two overlapping semicircles can be observed on the impedance spectra. The ratio of diameters of the semicircle in the high frequency region against the semicircle in the low frequency region tends to increase at higher overpotential.

The potential dependence of the parameters of the CPE (τ_2 and Φ) are illustrated in Figs 5 and 6, respectively. These parameters allow estimation of the double-layer capacitance by means of the equation suggested by Brug *et al.* [23]:

$$C_{dl} = \tau_2(1/R_S + 1/R_\infty)^{-(1-\Phi)/\Phi} \qquad (13)$$

The variation with overpotential of the calculated double-layer capacitance is shown in Fig. 7. The double-layer capacitance is almost constant with an average value $C_{dl} = 0.097\,F\,cm^{-2}$. For the RuO_2 an interfacial capacitance of 142 μF cm^{-2} (estimated by cyclic voltammetry) has been reported in the literature [9]; this was attributed to a combination of double layer effects and surface redox processes. This value allows calculation of a roughness factor of about 683 for the investigated electrodes which is in good agreement with the value found from the voltammetric measurements.

Since the experimental data for R_∞, R_P and C_P obtained at several values of potential can be expressed as functions of k_1, k_{-1}, k_2 and k_{-2} it is possible to estimate the above rate constants by an appropriate fitting procedure. Thus, using a nonlinear least squares technique the estimated rate constants are as follows: $k_1 = 6.3 \times 10^{-8}$, $k_{-1} = 8.9 \times 10^{-6}$,

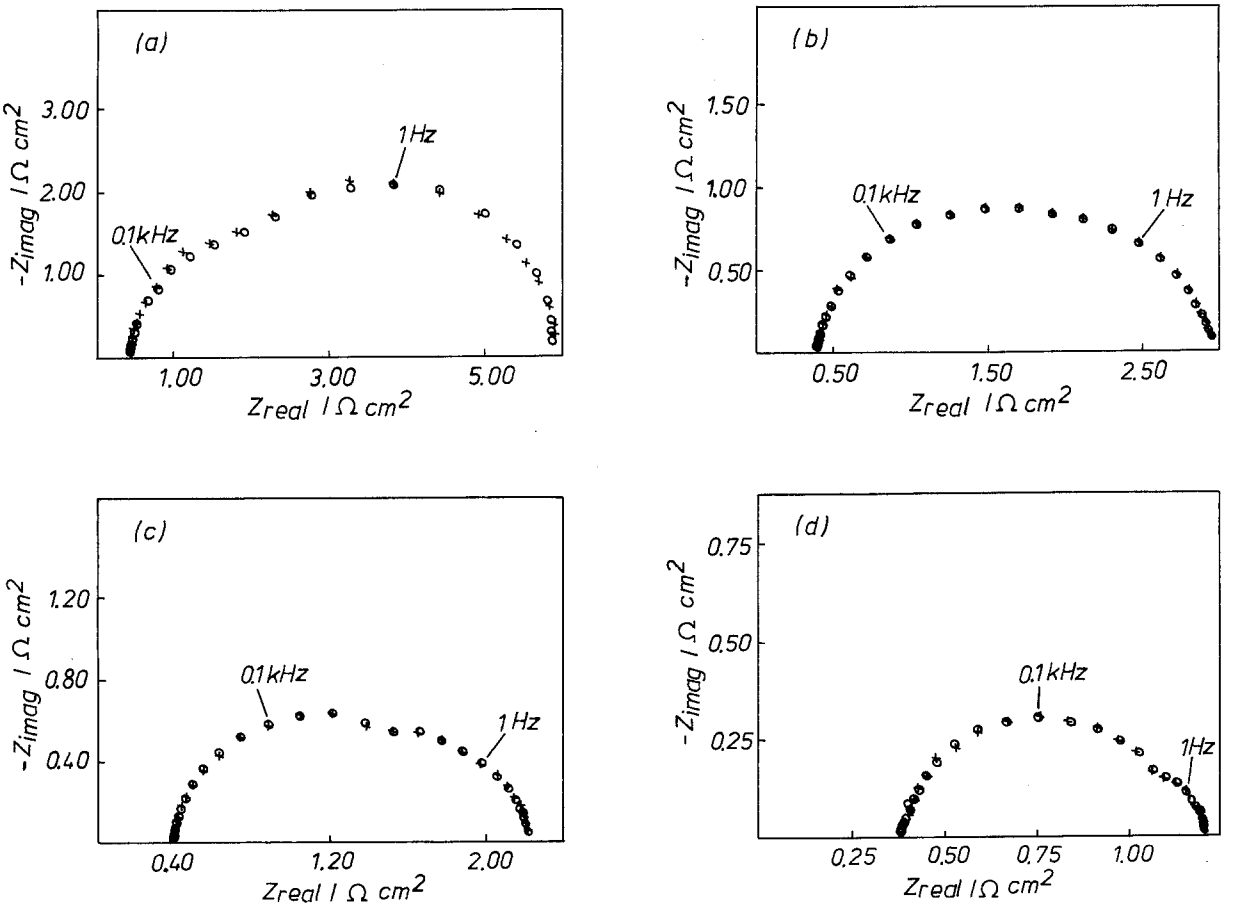

Fig. 4. Impedance spectra at several overvoltages for HER in 1 M NaOH on RuO_2. η: (a) −20, (b) −58, (c) −72 and (d) −84 mV. Key: (O) experimental data; (×) simulated values. Experimental conditions: 20 °C; frequency range: 3 kHz, 0.01 Hz; amplitude: 10 mV.

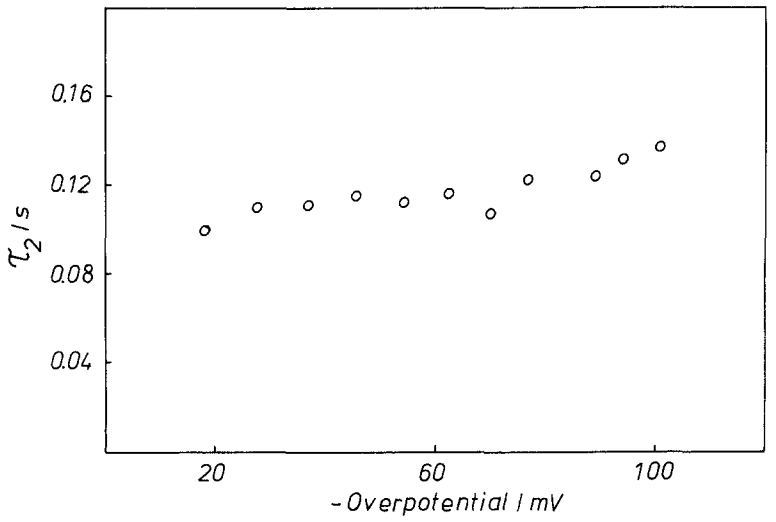

Fig. 5. The variation of the relaxation time (τ_2) as a function of η for HER on RuO_2 in 1 M NaOH.

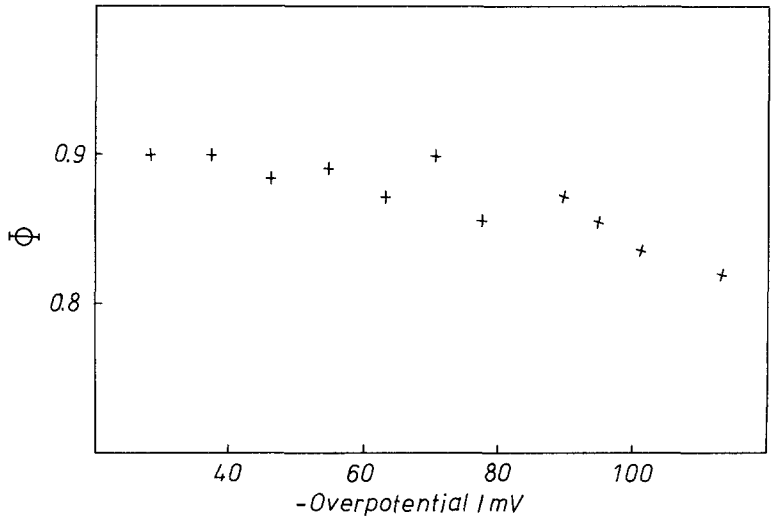

Fig. 6. The variation of the parameter of the CPE (Φ) as a function of η for HER on RuO_2 in 1 M NaOH.

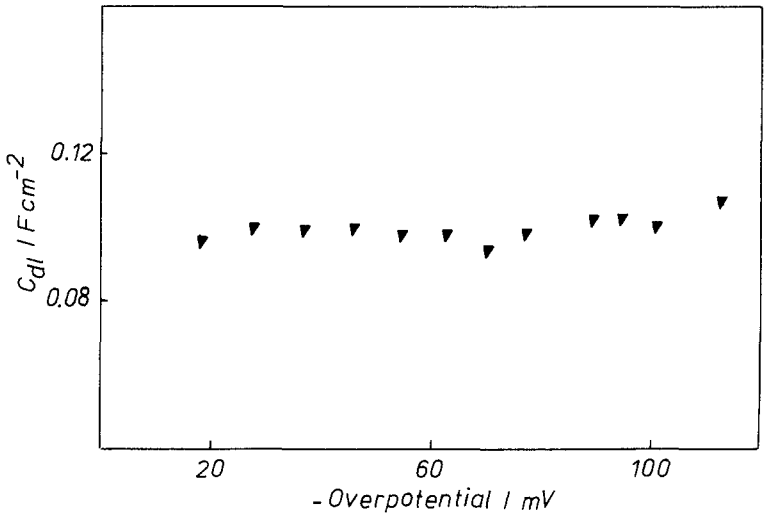

Fig. 7. Calculated C_{dl} values against η for HER on RuO_2.

$k_2 = 4.8 \times 10^{-7}$ and $k_{-2} = 3.4 \times 10^{-9}$. It is also possible to calculate the surface coverage (θ) of adsorbed hydrogen atoms as a function of the overpotential, which is illustrated in Fig. 8. The value of θ increases with decrease in the potential tending to a pseudo-plateau in the high overpotential range. The rather small values of θ are in agreement with the conclusions of the polarization studies.

From the same constant rates the current density has been also calculated as $i = -F(v_1 + v_2)$ Both the experimental and calculated potential dependence of current density are illustrated in Fig. 9. The slope of the calculated i against η curve is about 35 mV decade^{-1} in the low overpotential range while it is close to 75 mV decade^{-1} at overpotentials higher than 70 mV. The good agreement with the results of the polarization studies supports the idea that the mechanism of the HER in alkaline media on RuO_2 involves the Volmer and Heyrovsky steps (Equations 1 and 2).

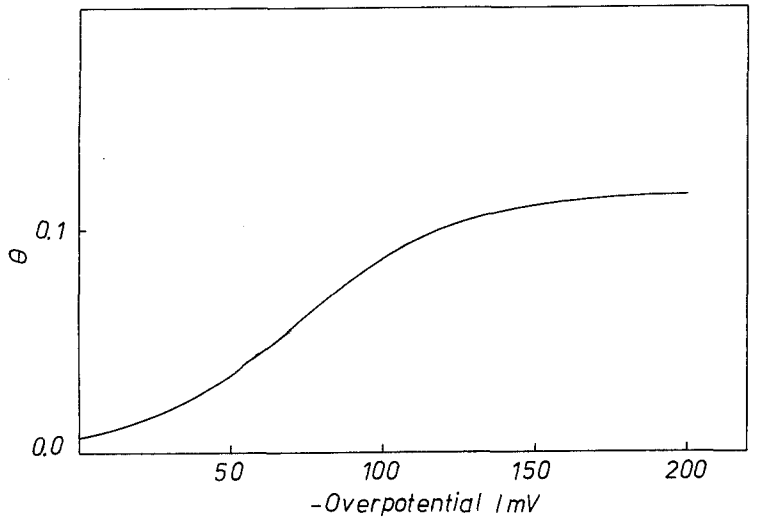

Fig. 8. Calculated variation of the surface coverage of adsorbed hydrogen atoms (θ) as a function of η.

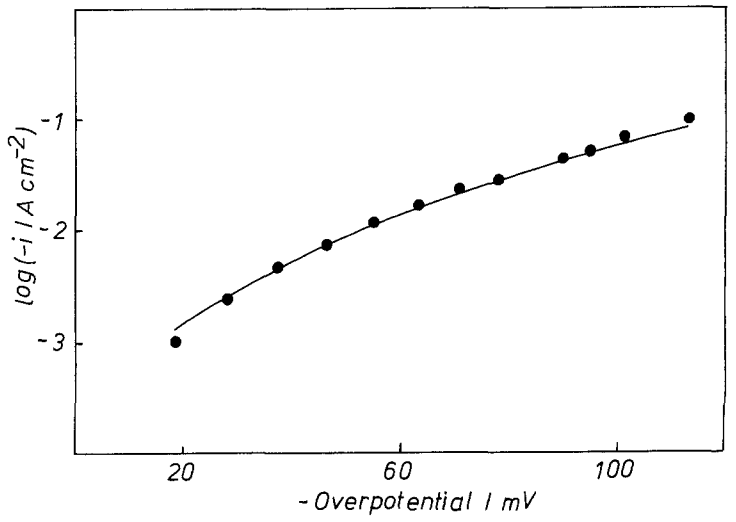

Fig. 9. Potential dependence of the current density of HER on RuO_2. Experimental values in 1 M NaOH (O); calculated from evaluated k_i values (solid line).

4. Conclusions

A study of HER in alkaline solution on RuO_2 coated nickel electrodes was performed with the purpose of obtaining new information about the mechanism and the kinetic parameters of the reaction. The cyclic voltammetry measurements, as well as the double-layer capacitance (evaluated by impedance measurements), allowed estimation of a roughness factor between 651 and 683 for an amount of 4.2 mg cm^{-2} RuO_2. The potentiostatic measurements suggest a mechanism for the HER which involves a charge-transfer reaction followed by an electrochemical desorption. The rate constants of the forward and backward reactions of Volmer and Heyrovsky steps have been estimated from the impedance measurements by a nonlinear fitting method.

References

[1] J. F. Cairns, D. A. Denton and P. A. Izard, *Eur. Pat. Appl. 129 374*, 5 Aug. (1984).
[2] A. Nidola, *PCT Int. Appl. 8 603 790*, 20 April (1986).
[3] J. Clerc-Renaud, F. Leroux and D. Ravier, *Eur. Pat. Appl. 240 418*, 4 June (1988).
[4] E. R. Kotz and S. Stucki, *J. Appl. Electrochem.* **17** (1987) 1190.
[5] M. Jaccaud, F. Leroux and J. C. Millet, *Mater. Chem. Phys.* **22** (1989) 105.
[6] M. Kleijn and H. P. Van Leeumen, *J. Electroanal. Chem.* **247** (1988) 253.
[7] S. Trasatti, 'Modern Chlor-Alkali Technology' (edited by T. C. Wellington), Elsevier, London (1992) p. 281.
[8] L. D. Burke and O. J. Murphy, *J. Electroanal. Chem.* **109** (1980) 99.
[9] *Idem, ibid*, **96** (1979) 19.
[10] *Idem, ibid*, **112** (1980) 39.
[11] I. M. Kodintsev and S. Trasatti, *Electrochim. Acta* **39** (1994) 1803.
[12] J. C. F. Boodts and S. Trasatti, *J. Appl. Electrochem.* **19** (1989) 255.
[13] C. Iwakura, M. Tanaka, S. Nakamatsu, H. Inoue, M. Matsuoka and N. Furukawa, *Electrochim. Acta* **40** (1995) 977.
[14] Th. Borucinski, S. Rausch and H. Wendt, *J. Appl. Electrochem.* **22** (1992) 1031.
[15] B. V. Tilak and C. P. Chen, *ibid.* **23** (1993) 631.
[16] T.-C. Wen and C.-C. Hu, *J. Electrochem. Soc.* **139** (1992) 2158.
[17] S. Trasatti, 'Electrochemistry of Novel Materials' (edited by J. Lipkowski and P. N. Ross), VCH, Weinheim (1994) p. 252.
[18] M. Okido, J. K. Depo and G. A. Capuano, *J. Electrochem. Soc.* **140** (1993) 127.
[19] R. D. Armstrong and M. Henderson, *J. Electroanal. Chem. Interf. Electrochem.* **39** (1972) 81.
[20] Y. Choquette, L. Brossard, A. Lasia and H. Menand, *J. Electrochem. Soc.* **137** (1990) 1723.
[21] R. L. Zeller and R. Savinell, *Corros. Sci.* **26** (1986) 591.
[22] B. A. Boukamp, 'Equivalent Circuit', University of Twente, The Netherlands (1989).
[23] G. J. Brug, A. L. G. Van der Eeden, M. Sluyters-Rehbach and J. H. Sluters, *J. Electroanal. Chem. Interf. Electrochem.* **176** (1984) 275.