

## SHORT COMMUNICATION

**Electrolytic resistance at a hydrogen-evolving nickel wire electrode**

J.-Y. HUOT\*

*Institut de recherche d'Hydro-Québec, 1800 montée Ste-Julie, Varennes, Québec, Canada J0L 2P0*

Received 16 August 1988; revised 26 September 1988

**1. Introduction**

Bubble formation at both electrodes during alkaline water electrolysis causes an additional ohmic drop, thus reducing the energy efficiency of the process. Minimizing gas bubble problems is therefore of practical interest.

The relation between layers of hydrogen bubbles and ohmic drop, their dependence on current density, the height of the electrode in the cell, the temperature and electrolyte concentration have all been investigated with different electrode materials [1, 2]. However, although the effects of the diameter [1] and height [2] of the disc or plate cathode have been examined, the effect of the cathode length on the ohmic drop and energy efficiency in the case of wire cathodes is not known. In the work described here, on vertical hydrogen-evolving nickel wires, the ohmic resistance is determined as a function of time, wire length and shape, at a constant electrode height in KOH 30 wt % at 70°C.

**2. Experimental details**

A polysulfone electrochemical cell was used with a nickel working electrode, nickel counter electrode and an external Hg/HgO/KOH 1 M reference electrode, which was immersed in the upper section of a Luggin capillary tube. The tip of the tube was kept at a constant distance ( $\approx 2$  mm) from the surface of the

working electrode, the latter consisting of a vertical 0.05-cm-diameter wire (Mat. Res. 99.99%), 1–6 cm in length, with a corresponding surface area ranging from 0.16 to 0.94 cm<sup>2</sup>. The samples were polished with 1  $\mu$ m alumina paste and rinsed with distilled water before being immersed in the KOH 30 wt % at 70°C. All solutions were purged with nitrogen prior to measurement.

The potential of the working electrode was controlled by a 1286 Electrochemical Interface (Solartron) and the impedance was measured with a 1250 Frequency Analyser (Solartron), both coupled to an HP-9000 controller. All potential values for the electrode are given with respect to the Hg/HgO/KOH 1 M reference electrode at 23°C. The measured value of the reversible potential for the hydrogen evolution reaction in alkaline solution at 70°C is  $-960$  mV with respect to this reference electrode.

**3. Results and discussion**

The intensity and time dependence of the current density at  $-1.40$  V vs Hg/HgO (non-*IR* corrected), i.e. approximately  $-400$  mV vs RHE, show a strong dependence on the electrode length or area, since the latter is directly proportional to the wire length (Fig. 1). It is postulated that this difference is due to the ohmic drop, which is the *RI* product (ohmic resistance with a resistance path of constant length (ohm cm<sup>2</sup>)  $\times$  current density (A cm<sup>-2</sup>)). Theoretically, it should be independent of the surface area, unless the ohmic resistance depends on the electrode length or shape.

The nickel cathodes were polarized at a constant hydrogen overpotential of  $-300$  mV vs RHE by computer-controlled feedback: the ohmic resistance between the Luggin tip and the upper section of the electrode surface is assumed to be equal to the real component of the impedance at 10 kHz, which is measured continuously, and the potential is adjusted around  $-1.3$  V to keep the overpotential constant. Under such experimental conditions, the ohmic resistance is given by the real component of the high-frequency impedance because the complex plane plot exhibits the classic Randles behavior (Fig. 2). From the experimental data, the electrode capacitance and the charge transfer resistance are found to be  $110 \mu\text{F cm}^{-2}$  and  $3.2 \text{ ohm cm}^2$ , respectively, and at frequencies higher than 10 kHz the impedance of the electrode double layer becomes negligible and the real

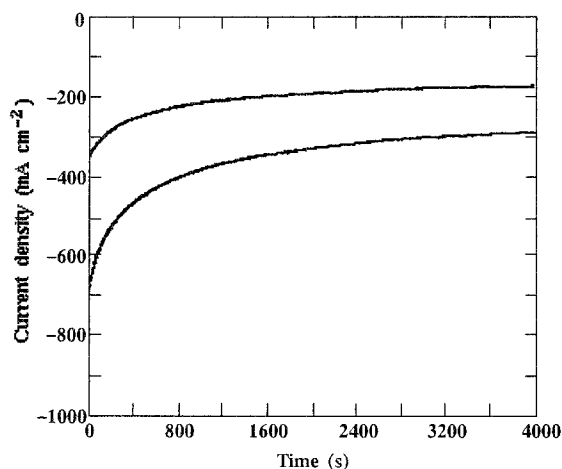


Fig. 1. Time dependence of the current density for a nickel cathode polarized at  $-1.40$  V vs Hg/HgO (non-*IR* corrected). The upper and lower curves are for 6 and 1 cm wire lengths, respectively.

\* Present address: Centre de Technologie Noranda, 240 Hymes Blvd., Pointe-Claire (Qué), Canada, H9R 1G5.

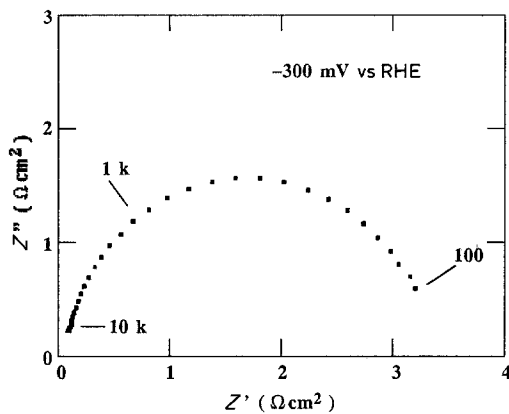


Fig. 2. Impedance diagram obtained at  $-300$  mV vs RHE ( $-1.3$  V vs Hg/HgO) on nickel electrode in 30 wt % KOH at  $70^\circ\text{C}$ . The length of the nickel wire is 1 cm.

component of the impedance equals the ohmic resistance  $\pm 0.01$  ohm  $\text{cm}^2$ .

Since the ohmic resistance is determined mainly by the bubble layer formed during intensive hydrogen evolution [1, 2], no straight dependence on the Luggin tip distance of the nickel electrode and the conductivity of the KOH solutions may be anticipated. A cell constant is therefore not established by measurements on a standard electrolyte in the absence of hydrogen evolution, and the absolute value of the high frequency ohmic resistance in the presence of hydrogen evolution is assumed to include the resistance of the electrolyte, the surface films, the gas bubbles and the circuit leads.

At  $-300$  mV vs RHE, the ohmic resistance is seen to be dependent on time and, also, on the electrode length or area (Fig. 3). Before it reaches the steady state at  $\approx 200$  s, it undergoes a relaxation process, which can be attributed to some reorganization taking place in the newly formed layer of bubbles [3]. The steady-state ohmic resistance ( $R_s$ ) is attained more rapidly than in the case of hydrogen on Pt cathodes in HCl solution [4].

The plot of the ohmic resistance vs  $t^{-1/2}$  (Fig. 4) reveals linear trends for all electrode lengths. The

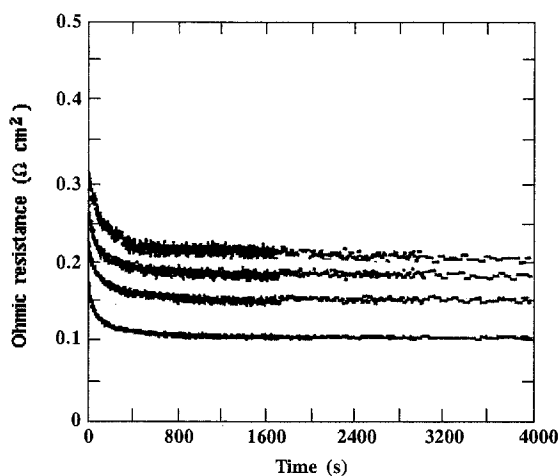


Fig. 3. Ohmic resistance decay for a nickel cathode polarized at a constant overpotential of  $-300$  mV vs RHE. From the top, the wire lengths are, respectively, 6, 4, 3 and 1 cm.

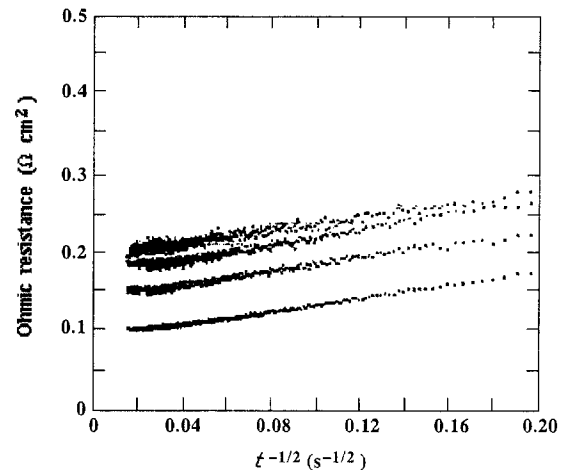


Fig. 4. Ohmic resistance vs  $t^{-1/2}$  for different wire areas. From the top, the wire lengths are, respectively, 6, 4, 3 and 1 cm.

common slope indicates that for the formation of the stationary bubble layer, all the electrodes reach the steady state at the same rate and by the same mechanism. In fact, it is known that the hydrogen gas is transferred to the bulk of 30 wt % solution by the diffusion/convection ( $\sim 40\%$ ) of dissolved gas as well as by bubbles departing from the electrode surface ( $\sim 60\%$ ) [5]. On the other hand, the growth of gas bubbles is determined by mass diffusion of the gas in the liquid and by hydrogen supersaturation at the bubble wall [6, 7] while the ohmic resistance appears to be proportional to the local gas fraction [6]. The foregoing considerations suggest that a diffusion phenomenon is involved in the relaxation process of the ohmic resistance. This means that hydrogen supersaturation would reach a maximum just after the cathodic overpotential is imposed, the dissolved hydrogen would diffuse at a distance from the electrode, and hydrogen supersaturation close to the electrode would decrease until it reached the steady-state value. This interpretation is supported by the decrease in the bubble population with the oxygen discharge time in 1 M KOH,  $30^\circ\text{C}$  [3].

A certain dependence of the ohmic resistance on the cathodic current density cannot be excluded however,

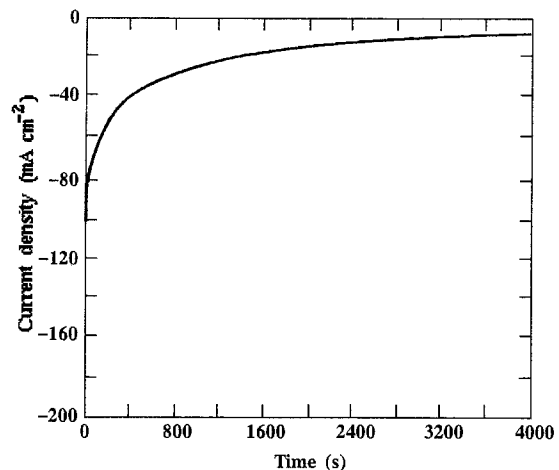


Fig. 5. Average current density-time dependence of a nickel cathode polarized at constant overpotential  $-300$  mV vs RHE.

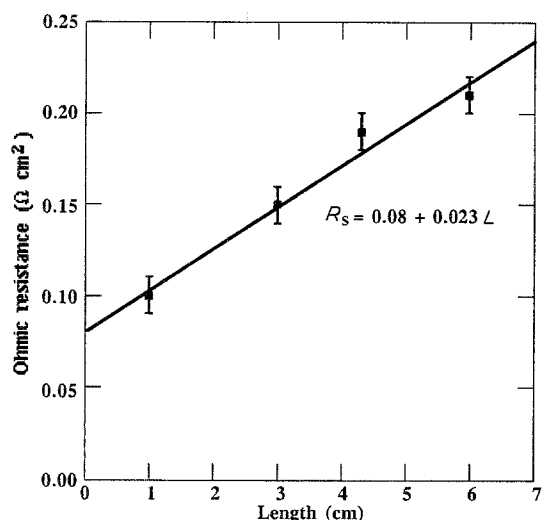


Fig. 6. Linear correlation between the steady-state ohmic resistance,  $R_s$ , and the nickel wire length.

since the deactivation process occurring during the first 100 s (Fig. 5) could result in a lower supersaturation [8]. Nevertheless, this effect remains relatively small, as suggested by the constant ohmic resistance as a function of current density [9] and by the difference in the resistance and current density time constants. A deactivation process has already been reported during a potentiostatic (non- $IR$  corrected) experiment under the same conditions [10].

The steady-state ohmic resistance ( $R_s$ ) as a function of the electrode length is not constant but increases linearly (Fig. 6). The resistance intercept can be associated with the ohmic resistance of the 30 wt % KOH electrolyte between the Luggin tip and the working electrode, which is estimated to be 0.5 ohm cm, i.e. of the order of the reported value [11]. Accordingly, the electrode-solution interface may be described as a series electrolytic resistance and a bubble layer resistance, where the bubble layer can be considered as a distribution of parallel local resistances, the observed value being determined by the lowest value(s).

These results indicate that longer electrode lengths call for a higher degree of screening (fraction of the electrode surface covered by the bubbles) of the nickel wire. The cumulative contribution of the bubbles sliding from the lower to the higher section of the wire results in an increase in the local resistance, although no attempt to detect a limiting value was made. The slope  $\partial R_s / \partial L = 0.023 \text{ ohm cm}$  suggests that the  $R_s$  value is mainly determined by the mean resistance of the electrode segment, for which  $R_s \approx 0.02 \text{ ohm cm}^2$ , i.e. the first cm of the nickel wire.

It has been pointed out that the electrolytic solution

around a gas-evolving electrode forms a fixed bubble layer, whose thickness equals the diameter of the adherent bubbles, and a diffuse layer [2, 5]. For hydrogen electrodes, the ohmic resistance is determined largely by the gas void fraction in the fixed layer [1, 2, 7]. Although this gas volume fraction increased with the electrode height in the cell, the ohmic resistance at  $200 \text{ mA cm}^{-2}$  changes only by +0.01 ohm for a height increment of 10 cm [2] and consequently it cannot account for the observed trend for  $R_s$  vs electrode length.

Dependence on the electrode shape may also be observed, since  $R_s = 0.28 \text{ ohm cm}^2$  for the U-shaped 6 cm electrode compared to  $0.21 \text{ ohm cm}^2$  for the linear 6 cm electrode. In agreement with the  $R_s$ -length relation, the ohmic resistance of a U-shaped 6 cm electrode is somewhat equivalent to that of a linear 3 cm electrode, showing that a U-shaped 6 cm electrode behaves like two independent linear 3 cm ones.

In summary, the length and shape dependency of the steady-state ohmic resistance for nickel wires emphasizes the importance of taking these parameters into account in the evaluation of electrocatalytic activity at high current densities. In experiments performed on wire electrodes of various lengths, the Tafel lines  $\log i - \eta$  must be corrected for the ohmic drop [10] but no typical value for the ohmic resistance can be assumed without inducing systematic errors in the Tafel parameters. For the steady state at  $-300 \text{ mV}$  vs RHE on a nickel cathode, the ohmic drop ranges from 2 to 4 mV.

## References

- [1] L. J. J. Janssen and E. Barendrecht, *Electrochim. Acta* **28** (1983) 341.
- [2] B. E. Bongenaar-Schlenter, L. J. J. Janssen, S. J. D. Van Stralen and E. Barendrecht, *J. Appl. Electrochem.* **15** (1985) 537.
- [3] L. J. J. Janssen, C. W. M. P. Sillen, E. Barendrecht and S. J. D. Van Stralen, *Electrochim. Acta* **29** (1984) 633.
- [4] J. A. Harrison and A. T. Kuhn, *Surf. Technol.* **19** (1983) 249.
- [5] L. J. J. Janssen and E. Barendrecht, *J. Appl. Electrochem.* **15** (1985) 549.
- [6] S. J. D. Van Stralen and W. M. Sluyter, *J. Appl. Electrochem.* **15** (1985) 527.
- [7] H. Vogt, in 'Comprehensive Treatise of Electrochemistry' (edited by E. Yeager, J. O'M. Bockris, B. E. Conway and S. Sarangapani), Plenum Press, New York (1983) Vol. 6, Ch. 7.
- [8] S. Shibata, *Denki Kagaku.* **44** (1976) 709.
- [9] P. Gallone, G. Modica and S. Maffi, *J. Electroanal. Chem.* **180** (1984) 421.
- [10] J.-Y. Huot and L. Brossard, *Int. J. Hydrogen Energy* **12** (1987) 821.
- [11] N. Nitabah, D. Lucasoli and P. Degobert, *Electrochim. Acta* **17** (1972) 327.