

Impedance peaks of sealed nickel/cadmium cells at low states-of-charge

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Abstract

The impedance of sealed nickel/cadmium cells is measured at low states-of-charge that correspond to a cell e.m.f. range of 0.0 to 1.3 V. The results show that the impedance exhibits a pronounced maximum between 0.3 and 0.45 V. It is concluded that the impedance maxima are due to physicochemical processes taking place at the nickel oxide electrode. The impedance of the nickel oxide electrode is dominated by three different phenomena: (i) a Ni(II)/Ni(III) reaction between 1.3 and 0.8 V; (ii) a double-layer impedance between 0.8 and 0.3 V; (iii) a hydrogen evolution reaction between 0.3 and 0.0 V.

Introduction

The impedance of sealed nickel/cadmium cells has been measured by several workers [1–10]. Except for one study [3], however, all measurements have been made at appreciable states-of-charge (SOCs) (> 10%) and at cell voltages above 1.3 V. The impedance of sealed nickel/cadmium cells in the c.m.f. range 0.0–1.3 V (equilibrium cell voltage) has not been reported in the literature.

When a sealed nickel/cadmium cell is discharged to very low SOC (< 0.1%), the cell e.m.f. undergoes a large change, from 1.3 to 0.0 V, for a negligible change in the SOC. This behaviour is due to a shift in the potential of the nickel oxide electrode since sealed cells are designed to be positive limited and the potential of the cadmium electrode remains constant (i.e., -0.91 V versus Hg/HgO at 25 °C). Thus, the interfacial potential of the nickel oxide electrode varies from $+0.39$ to -0.91 V versus Hg/HgO for a negligible change in its SOC.

Generally, the impedance of a nickel/cadmium cell consists of contributions from the nickel oxide electrode, the cadmium electrode, and the electrolyte. It is difficult, if not impossible, to separate out the contributions from the different electrodes in a general case. At low cell SOC, the SOC of the cadmium electrode is $\sim 40\%$ and the kinetics of the electrode reaction are very facile ($i_0 \approx 10^{-2}$ A cm⁻²) [11]. Thus, the impedance of the cell should be virtually equal to that of the nickel oxide electrode and the inter-electrode region (separator + electrolyte). The latter component can be separated out by simple techniques at low SOC.

In view of the above considerations, a programme was undertaken to study the impedance of sealed nickel/cadmium cells at low SOC. This was expected to yield

information regarding physicochemical processes occurring at the nickel oxide electrode. The impedance of the cells was measured in the cell e.m.f. range 0.0–1.3 V corresponding to a SOC of <0.1%. It should be emphasized that special procedures were adopted to reach such low SOCs and the measurements were made at (near) equilibrium conditions*.

Experimental

The impedance of sealed nickel/cadmium cells was measured using a Solartron frequency response analyser (FRA) in conjunction with an electrochemical interface (ECI). The impedance was determined in the series equivalent form ($R_s \pm j X_s$) by applying a signal of 1 mV (r.m.s.). The cells were kept in an environmental chamber that controlled the temperature to within ± 0.5 °C of the set value.

An experimental procedure to obtain reproducible results was established by undertaking preliminary studies with different modes of cell conditioning and different periods of polarization. In order to attain a near-zero SOC (<0.1%), an initially charged cell was discharged to 1 V at the 2-h rate, followed by a discharge across a 0.5 Ω resistor for 16 h. The cell was subsequently dead-shortened for 24 h, to remove all the charge, and then left at open-circuit for 24 h during which time the cell voltage recovered to ~ 1.2 V.

Before starting the test, the cell was shorted again across 0.5 Ω for 10 min and the cell voltage fell to below 10 mV. The cell was then potentiostatically polarized to 0.0 V and the excitation signal was applied to the cell 20 min later. The measurement of impedance was commenced after a delay of 20 s at each frequency.

After measurements at each cell e.m.f., which usually took about ~ 30 min, the cell was polarized to the next higher/lower e.m.f. and the procedure repeated. Tests were made from 0.0 to 1.3 V for increasing cell e.m.f. (forward sweep), generally in steps of 0.1 or 0.025 V**. After reaching 1.3 V, the cell was left at open-circuit overnight and the impedance measurements were resumed the next morning with decreasing cell e.m.f. (reverse sweep) from 1.3 to 0.0 V in steps of 0.1 V.

Impedance measurements were performed initially between 100 and 0.001 Hz with 5 steps per decade on a logarithmic scale. It was found that no extra information was obtained outside a frequency range of 10 to 0.01 Hz. Hence, further tests were mainly performed over this frequency range, with occasional runs from 1 Hz to 0.01 Hz. Measurement at 20 Hz was performed at each cell e.m.f. in order to determine the ohmic part of the cell impedance.

Impedance studies were conducted on several cells having the same capacity, on cells with different capacities, and on cells from different manufacturers in order to confirm that the results were generally applicable to all sealed nickel/cadmium cells, and not specific to a particular size or design.

Several impedance measurements were also made on 'test' cells constructed from one positive plate and two negative plates in 30% KOH. The respective impedances

*When a cell is discharged to 1 V, the SOC is $\sim 10\%$ even though no capacity is available at useful discharge rates. Very low SOCs can be achieved by discharging across a resistor to about 10 mV, followed by a long duration of dead-shortening of the cell. Some workers have considered discharge to 1 V itself as 'zero' SOC; this may be misleading.

**'Forward' and 'reverse' sweeps mean that the cell impedance was measured at 0 V, 0.1 V, etc. up to 1.3 V for increasing and decreasing cell e.m.f., respectively. This should not be confused with the continuous potential sweeps applied in cyclic voltammetric studies.

of the total cell, the nickel oxide electrode and the cadmium electrode were measured separately. This confirmed that the cell impedance at low SOC is practically equal to that of the nickel oxide electrode after correcting for the resistance due to the separator and the electrolyte.

In order to study the effect of the nylon separator, impedance of a test cell was determined with and without nylon separator extract added to the electrolyte. The extract was prepared by boiling the separator material in 30% KOH for about 4 h. The addition of the extract caused no significant change in the impedance characteristics. The effect of decarbonation of the electrodes and the electrolyte was studied in a similar manner. Again, no change in impedance behaviour was observed.

In this paper, the impedance data gathered from a 12-A h sealed nickel/cadmium cell is presented as typical behaviour. The measurements were performed at -10 , 0 , $+10$, $+20$ and $+30$ °C. Only, the results obtained at $+20$ °C are reported to highlight the basic findings.

Results and discussion

Figure 1 shows the plot of the resistive component (R_S) of the cell impedance at 1, 0.1 and 0.01 Hz, as a function of the cell e.m.f. (V^T). Figure 2 gives a plot of the reactive component (X_S) of the cell impedance at 1, 0.1 and 0.01 Hz as a function of cell e.m.f. The following features can be observed.

(i) R_S at 0.01 Hz (Fig. 1) shows a peak at ~ 0.375 V in the forward sweep; the peak value is ~ 35 times greater than the lowest value. Similarly, at 0.1 Hz, R_S exhibit a peak at ~ 0.3 V in the forward sweep with a value ~ 29 times the lowest value. At 1 Hz, however, R_S decreases monotonically with an inflexion between 0.2 and 0.3 V in the forward sweep.

(ii) In the reverse voltage sweep, R_S at 0.01 and 0.1 Hz reaches peak values at 0.15 and 0.1 V, respectively, and displays a hysteresis of ~ 0.2 V in the cell e.m.f. at which peak values of R_S occur. Further, the peak value of R_S in the reverse voltage sweep is higher than that in the forward sweep.

(iii) At 1 Hz, R_S yields a small local maximum in the reverse voltage sweep; this is less than the value of R_S in the forward voltage sweep for a major part of the cell e.m.f. range.

(iv) At all frequencies, R_S remains nearly constant between 0.9 and 1.3 V and reaches the same value, irrespective of the direction of the voltage sweep.

(v) The value of R_S at $V^T=0.0$ V is the same, irrespective of the direction in which it is reached at 0.1 and 0.01 Hz.

(vi) In the frequency range 0.01 to 0.1 Hz, R_S is decreased by an order of magnitude for a decade increase in frequency.

(vii) As with R_S , X_S (Fig. 2) exhibits peaks around a cell e.m.f. of 0.45 V at all frequencies in the forward voltage sweep. The peak value is about 25 to 50 times larger than the minimum value.

(viii) In the reverse voltage sweep at all frequencies, the peak value of X_S is higher than that in the forward sweep. The cell e.m.f. at which peak in X_S occurs displays a hysteresis of about 0.15 V.

(ix) In the cell e.m.f. range 0.8–1.3 V, the value of X_S is the same, irrespective of the direction of the voltage sweep. Furthermore, X_S reduces by an approximate order of magnitude for every decade increase in frequency.

(x) At $V^T=0.0$ V, the value of X_S is the same, irrespective of the direction in which it is reached.

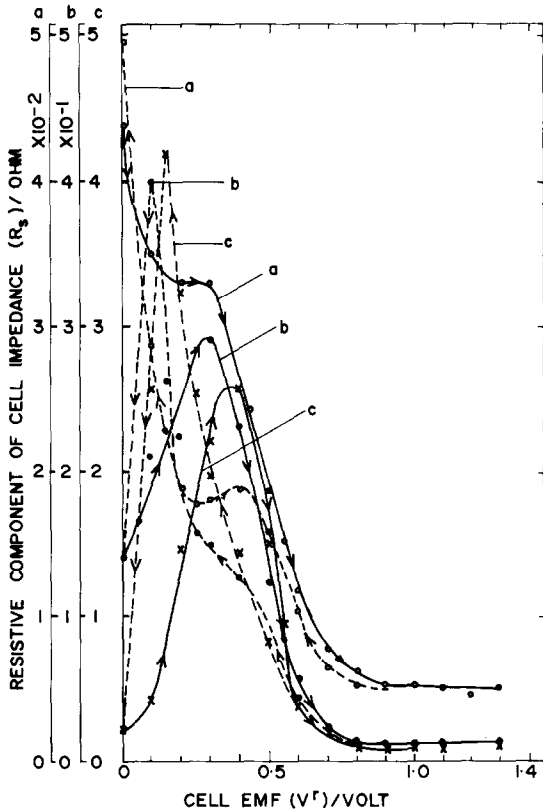


Fig. 1. Variation of resistive component (R_s) of cell impedance with cell e.m.f. (V) for forward (\rightarrow) and reverse ($\leftarrow\leftarrow\leftarrow$) voltage sweeps at: (a) 1 Hz, (b) 0.1 Hz, (c) 0.01 Hz; 12-A h sealed nickel/cadmium cell at 20 °C.

At this stage, it is appropriate to consider why the above observations, especially the occurrence of R_s and X_s maxima at a cell e.m.f. of about 0.4 V, have not been reported in previous literature. Probable explanations may be as follows.

(a) Impedance measurements were made primarily at either 0.0 V (i.e., zero SOC) or at voltages above 1.3 V (i.e., at relatively high SOC).

(b) Measurements were not made in the 'knee' region of the cell e.m.f. versus SOC curve, nor, at close intervals of cell e.m.f.

(c) The impedance measurements were not made at negligible nor small departures from equilibrium conditions, unlike in the present study.

As pointed out earlier, and confirmed by experiment, the appearance of impedance maxima for sealed nickel/cadmium cells is attributable to physicochemical processes at the nickel oxide electrode, and not at the cadmium electrode. Furthermore, since studies on test cells showed that the impedance features were unaffected by the presence of nylon hydrolysate or carbonates in electrodes and electrolyte, it can be concluded that the appearance of impedance maxima is associated with the general behaviour of the sintered nickel oxide electrodes, and is not associated with carbonates in the electrolyte or adsorption of the products of nylon hydrolysis on the electrode.

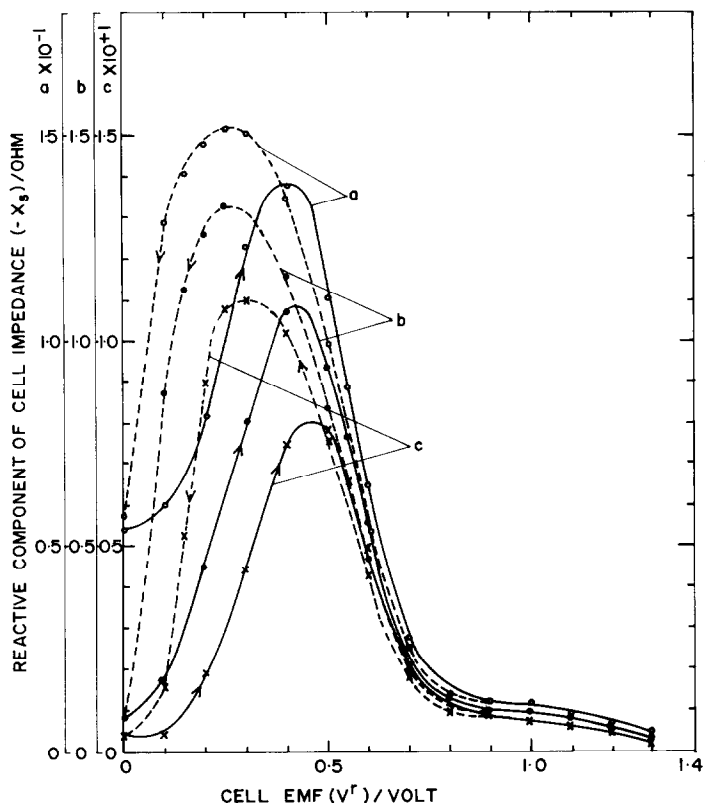


Fig. 2. Variation of reactive component (X_s) of cell impedance with cell e.m.f. (V^r) for forward (—) and reverse (---) voltage sweeps at: (a) 1 Hz, (b) 0.1 Hz, (c) 0.01 Hz; 12-A h sealed nickel/cadmium cell at 20 °C.

In order to further understand the nature and cause of the impedance maxima, the impedance of the cell was plotted in the complex plane for various cell e.m.f.s. The data are presented in Figs. 3–6 from which the following observations can be made.

(1) At a cell e.m.f. of 1.3 to 1.2 V, the complex plane plots show a fairly well defined curvature of circular arc. This is indicative of a charge-transfer-controlled Faradaic reaction. This is probably the Ni(III)/Ni(II) reaction (Figs. 3 and 5).

(2) When V^r is between ~ 1.1 V and ~ 0.4 V, the complex plane plots of the cell impedance are practically linear. The slope of the straight line increases with decrease in the cell e.m.f. and is about 85° at 0.8 V. Between 0.6 and 0.4 V, the slope of the impedance plots decreases (Fig. 4).

(3) Below a cell e.m.f. of about 0.4 V, the complex plane plots begin to show a curvature. Below 0.2 V, a clear circular arc is observed. The re-appearance of a circular arc is indicative of a Faradaic reaction at these values of cell e.m.f.

In order to investigate further the nature of the cell impedance between the cell e.m.f.s of 0.2 and 0.0 V, complex plane plots were constructed at 25 mV intervals. These plots are presented in Fig. 6. It can be seen that the diameter of the semi-circular region decreases as $V^r = 0.0$ V is reached. This suggests that the charge-

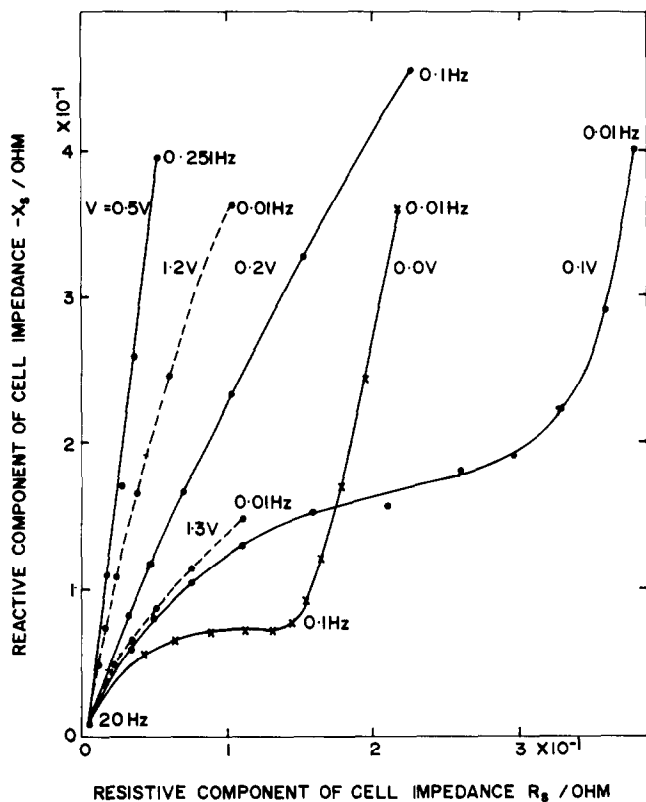


Fig. 3. Complex plane plot of cell impedance at different cell e.m.f.s at 20 °C; 12-A h sealed nickel/cadmium cell. Cell e.m.f. (V) and frequencies are shown on curves.

transfer resistance of the electrode reaction decreases as 0.0 V is approached. Thus, it may be concluded that the standard potential of the (as yet unidentified) reaction occurring at the nickel oxide electrode is around 0.0 V versus Cd/Cd(OH)₂ (or 0.905 V versus Hg/HgO) at 20 °C.

Factors affecting cell impedance

The above findings have revealed interesting trends that have not been reported in the literature. They may be summarized as follows. The cell e.m.f. range 0.0 to 1.3 V, can be divided into three separate regions.

(i) Above 1.1 V, where the impedance of the cell is mainly due to the Faradaic impedance of Ni(III)/Ni(II) reaction.

(ii) Between 1.0 and 0.2 V, where the impedance of the cell (and hence, the impedance of the nickel oxide electrode) is due to the double layer at the nickel oxide electrode. The slope of the straight lines in the complex plane plots is indicative of the losses associated with the double-layer impedance.

(iii) Below ~0.2 V, where a new, hitherto unsuspected, Faradaic reaction is occurring. This new reaction is responsible for the decrease in the cell impedance as 0.0 V is approached.

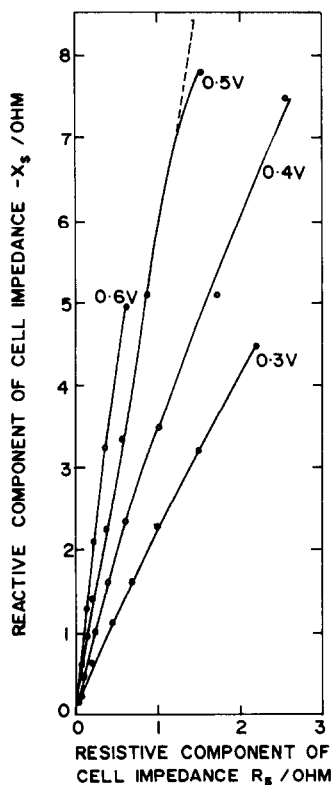


Fig. 4. Complex plane plot of cell impedance at different cell e.m.f.s in frequency range 1–0.01 Hz at 20 °C; 12-A h sealed nickel/cadmium cell. Cell e.m.f. (V^r) shown on curves.

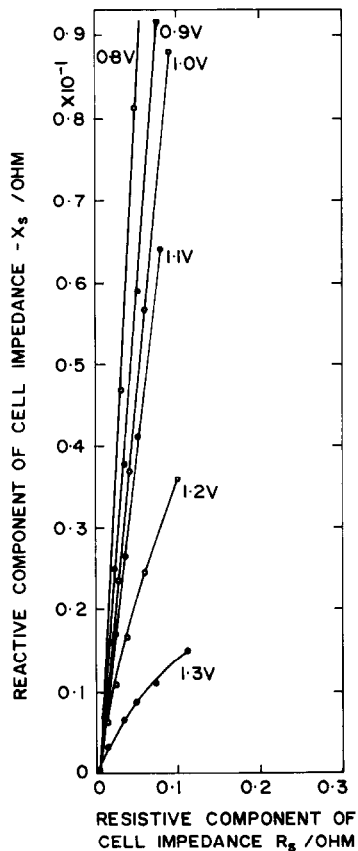


Fig. 5. Complex plane plot of cell impedance at different cell e.m.f.s in frequency range 1–0.01 Hz at 20 °C; 12-A h sealed nickel/cadmium cell. Cell e.m.f. (V^r) shown on curves.

Reaction at $V^r = 0.0$ V

When a sealed nickel/cadmium cell is discharged and maintained at 0.0 V, the potential of the nickel oxide electrode is 0.0 V versus Cd/Cd(OH)₂ (or –0.91 V versus Hg/HgO at 25 °C), as stated earlier. The reversible potential of the hydrogen electrode reaction (HER) is –0.02 V versus Cd/Cd(OH)₂ (–0.93 V versus Hg/HgO) at 1 atm., 25 °C and 30% KOH [12, 13]. Since, the potential of the nickel oxide electrode is close to the potential of the HER, it is reasonable to suppose that the HER will be sustained at a cell e.m.f. of 0.0 V. Using the Nernst equation, the equilibrium partial pressure (P^r_{H}) of hydrogen at $V^r = 0.0$ V yields a value of 0.07 atm. at 25 °C [13]. Similar calculations show that the cell e.m.f. is 0.143 and 0.202 V at hydrogen partial pressures of 10^{-6} and 10^{-8} atm., respectively. Now, it is generally accepted that the presence of hydrogen may be detected down to a partial pressure of 10^{-8} atm. [14]. In addition, the equilibrium coverage of adsorbed hydrogen on platinum at this partial is about 0.04 in H₂SO₄ [14]. It may be expected that even on nickel in contact with KOH, a similar coverage is possible. Thus, it is reasonable to assume that the HER

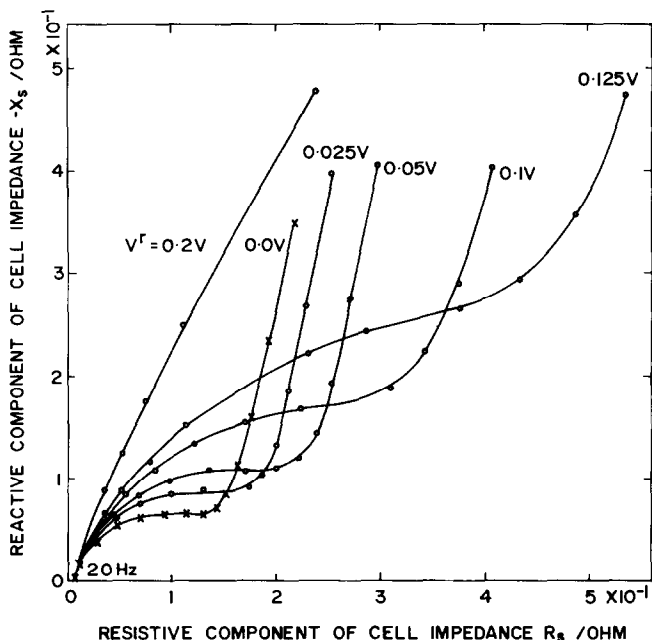


Fig. 6. Complex plane plot of cell impedance around $V^r = 0.0$ V in frequency range 20–0.01 Hz at 20 °C. Cell e.m.f. shown on curves. Except at $V^r = 0.2$ V, lowest frequency is 0.01 Hz.

is detectable at a nickel oxide electrode upto a cell e.m.f. of 0.2 V in sealed nickel/cadmium cells.

An implication of the above discussion is that hydrogen is present at low pressures in sealed nickel/cadmium cells stored in a discharged, shorted mode. Further, as the cell voltage recovers to values above 0.2 V, the hydrogen is removed completely by ionization.

Cadmium hydroxide migrates from the cadmium electrode to the nickel oxide electrode when sealed nickel/cadmium cells are subjected to charge/discharge cycling. Hence, it is necessary to consider the possibility of the $\text{Cd}/\text{Cd}(\text{OH})_2$ reaction occurring on the nickel oxide electrode at a cell e.m.f. of 0.0 V. Nevertheless, because of the fast kinetics of the cadmium electrode reaction, the latter cannot be sustained at overpotentials beyond ~ 25 mV. Thus, the charge-transfer resistance must increase to a very high value around $V^r = 25$ mV. On the other hand, the results given in Fig. 6 show that the charge-transfer resistance is low even at $V^r = 0.1$ V. Thus, it may be concluded that the Faradaic reaction occurring around $V^r = 0.0$ V in a sealed nickel/cadmium cell is the HER and not $\text{Cd}/\text{Cd}(\text{OH})_2$.

Modelling of impedance spectra

The HER could occur via either Volmer–Tafel mechanism or Volmer–Heyrovsky mechanism. It can be shown, however, that for either of these mechanisms, the Faradaic impedance can be represented by a series combination of the charge-transfer resistance (R_{CT}), the Warburg impedance (W) and the adsorption pseudo-impedance (R_A, C_A) [15]. The equivalent circuit representing the Faradaic impedance, together with the

double-layer impedance, is shown in Fig. 7. The double-layer impedance has been represented by a combination of resistors and capacitors.

From the measured impedance spectra of a 12-A h sealed nickel/cadmium cell at 0.0 V and 20 °C, values of the elements of the equivalent circuit were calculated. They are shown in Fig. 8. The experimental results and the fit given by the equivalent circuit are plotted in Fig. 9. A good fit is obtained.

From the calculated values of the circuit elements in the equivalent circuit fit, the exchange current density of the HER was found to be $1.34 \times 10^{-7} \text{ A cm}^{-2}$, based on true area. This value compares well with other values reported in the literature [16]. It may be observed from Fig. 8 that the impedance plot of the chosen equivalent circuit fits well with the experimental results over the entire frequency range. In particular, this equivalent circuit explains why the slope of the near-linear region is greater than 45°. Contrary to earlier conclusions, the linear region is not due to diffusion but to adsorption pseudo-impedance.

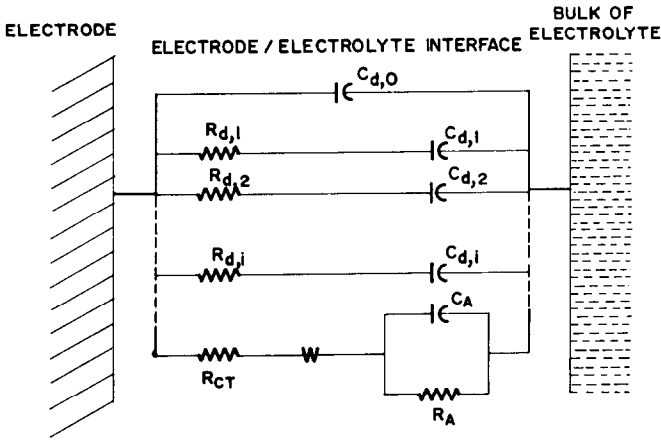


Fig. 7. Equivalent circuit for processes occurring at the nickel oxide electrode of a sealed nickel/cadmium cell around cell e.m.f. (V') of 0.0 V. $R_{d,1}$, $R_{d,2}$, $R_{d,i}$ and $C_{d,0}$, $C_{d,1}$, $C_{d,2}$, $C_{d,i}$ represent components of non-Faradaic-impedance. R_{CT} , W , C_A and R_A represent components of Faradaic impedance.

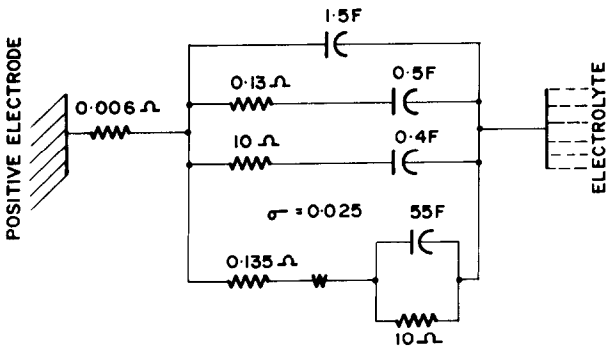


Fig. 8. Equivalent circuit that fits experimental results at $V'=0.0$ V in frequency range 0.01–10 Hz at 20 °C; 12-A h sealed nickel/cadmium cell.

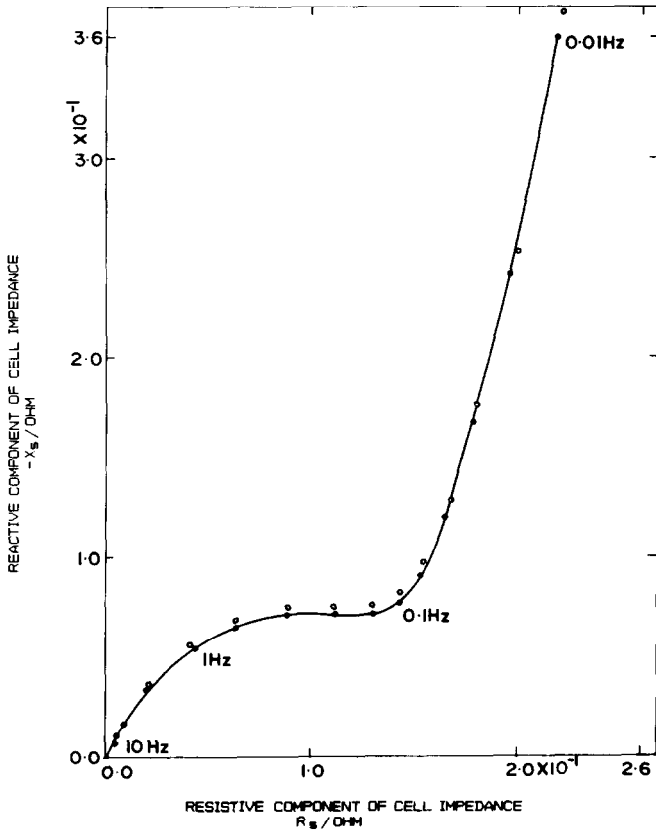


Fig. 9. Comparison of fit given by equivalent circuit (○) with experimental results (●) at cell e.m.f. of 0.0 V in frequency range 0.01–10 Hz at 20 °C; 12-A h sealed nickel/cadmium cell.

Conclusions

Maxima have been detected in the impedance of sealed nickel/cadmium cells. Three regions of the cell e.m.f. where different processes dominate have been identified. It has been shown that the HER occurs at $V^i \approx 0.0$ V. Further, an equivalent circuit, based on the occurrence of the HER at cell e.m.f. of 0.0 V, has been developed to completely represent the experimental results. The value of the exchange current calculated from the equivalent circuit is reasonably close to reported values.

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