

## Double-layer impedance of a nickel oxide electrode at low states-of-charge

M.S. Suresh

*ISRO Satellite Centre, Bangalore (India)*

(Received April 29, 1993; accepted May 28, 1993)

### Abstract

The double-layer impedance of a porous electrode is generally modelled by a transmission-line model or by invoking fractal geometry. In a nickel oxide electrode at low state-of-charge, however, the porosity does not affect significantly the impedance of the electrode below 100 Hz. Even then, the double-layer impedance cannot be represented by a pure capacitor. The reasons for this are to be found in the physical nature of the impregnated active material. Based on a phenomenological theory, the double-layer impedance can be modelled by a set of resistor/capacitor elements connected in parallel.

### Introduction

The impedance of an interface at which a Faradaic reaction occurs can, in the simplest case, be represented by a charge-transfer resistance ( $R_{ct}$ ) in parallel with a double-layer capacitance ( $C_d$ ). The impedance spectrum of such an interface is a semicircle of diameter  $R_{ct}$ . In a practical situation, however, such a simple equivalent circuit does not fit the experimental results. For example, the impedance spectrum of a porous battery electrode is a distorted semicircle.

If the potential of the interface is such that a Faradaic reaction is not possible, then the double-layer impedance can be represented, in the ideal case, by a single capacitor with an impedance spectrum that is a line parallel to the  $y$ -axis. At practical interfaces, however, the double-layer impedance can have both resistive and reactive components.

Generally, the distortion of the impedance spectrum is caused by the roughness, or porosity, of the electrode surface. Porous electrodes are often modelled as semi-infinite cylindrical pores using the transmission-line model [1]. Nevertheless, it is well known that the shape of the pores is ill-defined. Recently, the porous structure of electrodes has been modelled by invoking fractal geometry [2]. If the impedance of a planar electrode is  $Z$  (in the present discussion diffusion has been neglected and the reaction is assumed to be dominated by charge transfer), then the impedance of a porous electrode of the same material can be written as:

$$Z_p = Z^a \quad (1)$$

where:  $a = 1(D_f - 1)$ ;  $D_f$  is the fractal dimension.

A general equation of the above type can mathematically represent most of the situations and explain the distortions of the impedance spectrum. There are situations, however, where distortions of the impedance spectrum are not due to porosity of the

electrode. One such case is the impedance spectrum of a porous nickel oxide electrode at low states-of-charge.

**Effect of porosity on the impedance of nickel oxide electrode at low states-of-charge**

The impedance of an electrode/electrolyte interface is measured between the bulk of the electrode and the bulk of the electrolyte. In a porous electrode, the voltage drop due to the current flowing in the interior of the pores causes a non-uniform polarization of the interface. The extent of non-uniformity depends on the resistance of the electrolyte. Assuming a pure capacitive interfacial impedance ( $X$ ) at a planar electrode, it can be shown that the overall impedance of an electrode with cylindrical pores is a function of the ratio of the resistance of the electrolyte ( $R$ ) in the pore to the capacitive reactance of the pore ( $X$ ) (Table 1). If  $R/X=0.1$ , then the magnitude and phase differences between the planar electrode and the porous electrode are 0.5% and 1.75°, respectively. (Note, all impedances are for true area and not geometric area.)

An electrode in a typical cell is about 0.7 mm thick (manufacturer's data) and has pores ranging from 5 to about 50  $\mu\text{m}$  in diameter. The average pore size is about 15  $\mu\text{m}$  [3]. For a single pore of cylindrical shape, with a length equal to half the electrode thickness, the capacitive reactance of the pore is:

$$X = \frac{1}{2\pi fC} = \frac{1}{2\pi^2 fdlc} \tag{2}$$

where  $c$  is the double-layer capacitance per unit area, whose value is about 20 F/cm<sup>2</sup>;  $f$  is the frequency of measurement;  $l$  is the length of the pore;  $d$  is the diameter of the pore.

The resistance ( $R$ ) of the electrolyte in a typical pore is:

$$R = \frac{1}{K} \times \frac{4l}{\pi d^2} = 3.3 \times 10^4 \, \Omega \tag{3}$$

TABLE 1

Error in the impedance of an electrode by neglecting the effect of porosity, for: (a) a pure resistive interfacial impedance ( $Z=r$ ); (b) a pure capacitive interfacial impedance ( $Z_0=1/\omega c$ )

$R/Z$	$Z \ (\Omega)$		$Z_0 \ (\Omega)$	Error (%)
(a)				
0.01	1		1.003	0.3
0.1	1		1.033	3.3
1.0	1		1.313	31.3
$R/Z$	$Z \ (\Omega)$	$Z_0 \ (\Omega)$	Magnitude (%)	Phase (°)
(b)				
0.01	$-j1$	$3.5 \times 10^{-5} - j0.9996$	0.1	0.10
0.1	$-j1$	$0.0315 - j1.002$	0.5	1.75
1.0	$-j1$	$0.334 - j1.0312$	17.5	7.90

where:  $K$  is the conductivity of the electrolyte, which is  $0.6 \Omega^{-1} \text{ cm}^{-1}$  for 31% KOH at  $20^\circ \text{C}$  [3]. The ratio  $R/X$  is maximum when  $X$  is minimum. The interfacial reactance,  $X$ , is lowest at the highest frequency of measurement, i.e., 10 Hz in this work. The value of  $X$  of a typical electrode pore at 10 Hz is  $4.8 \times 10^6 \Omega$ .

The above calculations show that the resistance of electrolyte in the pore is 150 times smaller than the pore interfacial reactance at  $20^\circ \text{C}$ , below 10 Hz. At  $-10^\circ \text{C}$ , the resistance of the electrolyte in the pore,  $R$ , is  $7.6 \times 10^4 \Omega$ ; this is about 50 times smaller than the interfacial reactance. Thus, it is evident that the error in impedance caused by the assumption that the electrode is planar is less than 1% in magnitude and  $2^\circ$  in phase. The electrode area to be considered is, however, the true area and this is about 100 to 150 times the geometric area. The above calculations show that the porosity of the nickel oxide electrode does not significantly affect its impedance at frequencies below 10 Hz.

If a Faradaic reaction is taking place at the electrode pore, then the interfacial impedance is composed of a double-layer impedance in parallel with the Faradaic impedance. In the simplest case, the Faradaic impedance can be represented by a charge-transfer resistance,  $R_{\text{ct}}$ . For an electrode with  $15 \mu\text{m}$  pores, the interfacial resistance due to the Faradaic reaction is:

$$R_{\text{ct}} = \frac{RT}{AFi_0} = \frac{1.5 \times 10^2}{i_0} \quad (4)$$

where  $R$  = gas constant;  $T$  = temperature;  $A$  = area of pore;  $i_0$  = exchange current density.

Thus, until  $i_0$  is larger than  $5 \times 10^{-4} \text{ A cm}^{-2}$ ,  $R_{\text{ct}}$  is 10 times greater than  $R$  (pore). Since,  $i_0$  for the hydrogen-evolution reaction (HER) is about  $1 \times 10^{-6} \text{ A cm}^{-2}$ , the effect of porosity can be neglected if the HER is taking place at the nickel oxide electrode.

The impedance of a sealed nickel/cadmium cell at low states-of-charge (i.e.,  $< 0.1\%$ ) depends on the cell voltage. It has been shown that the impedance of the cell at low states-of-charge is predominantly due to the nickel oxide electrode. Further, in the voltage range 0.0 to 0.3 V, HER occurs at the nickel oxide electrode that has an impedance that is in parallel with the double-layer impedance. Above 0.3 V and up to  $\sim 1.0$  V, the impedance is due only to the double layer [4]. Figures 1 to 3 show the impedance of a 12 Ah nickel/cadmium cell at low states-of-charge and a cell voltage of 0.0, 0.5 and 1.0 V, respectively. At 0.0 V, the impedance in the charge-transfer region is a distorted semicircle. At 0.5 V and 1.0 V, the double-layer impedance is not purely capacitive, but has a resistive part. These observations indicate that the double-layer impedance of a nickel oxide electrode is not a pure capacitor.

As shown in the previous section, the porosity of a nickel oxide electrode does not effect the impedance of the electrode at low states-of-charge. The deviations from the ideal planar electrode impedance spectrum can be explained from a different point of view.

### Effect of state-of-charge on double-layer impedance

The nickel oxide electrode in a nickel/cadmium cell is manufactured by impregnating the pores of a porous nickel electrode with active material. The thickness of the nickel hydroxide deposited inside the pores is not uniform but depends on the impregnation process. The physical situation is shown schematically in Fig. 4.

A discharged nickel oxide electrode contains mainly nickel hydroxide,  $\text{Ni}(\text{OH})_2$ , which is a poor electronic conductor. Since the thickness of nickel hydroxide is not

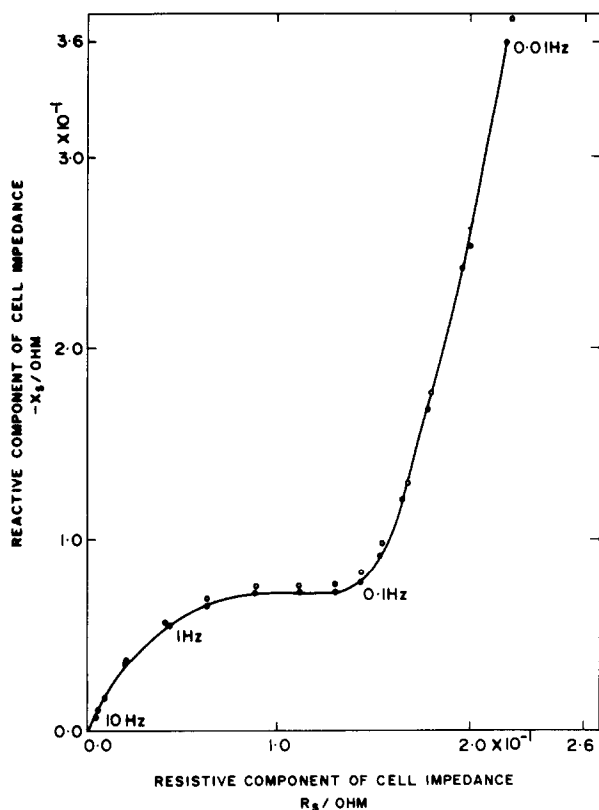


Fig. 1. Impedance spectrum of a 12 Ah nickel/cadmium cell at a cell voltage of 0.0 V (●). Calculated impedance spectrum from an equivalent circuit is also shown for comparison in the same frequency range (○).

uniform inside the pores, the resistance between the equipotential surfaces inside the bulk of the electrode and the bulk of the electrolyte varies from location to location inside the pores. By dividing the active-material/electrolyte interface region into small elemental areas ( $a_i$ ), the impedance between the electrolyte and the electrode can be represented by an infinite set of double-layer capacitors ( $C_{di}$ ) and their associated resistors ( $R_{di}$ ), as shown in Fig. 5. The values of the resistors depend upon the resistance of the  $\text{Ni}(\text{OH})_2$  layer associated with the elemental area ( $a_i$ ). When such a combination of resistors and capacitors is represented by a series resistor ( $R_s$ ) and a capacitor ( $C_s$ ), they become functions of frequency.

In the light of the above discussion, the double-layer impedance of a nickel oxide electrode can be represented by the equivalent circuit shown in Fig. 5. In such a circuit, at least one capacitor should have zero series resistance. This capacitor ( $C_{do}$ ) corresponds to the area of the electrode that is not covered by impregnated  $\text{Ni}(\text{OH})_2$ , but only by a thin passive film of hydroxide (1–2 Å) due to corrosion of nickel in alkaline solution. The resistance due to electron flow in this area is negligible due to quantum mechanical tunnelling.

In general, the elemental capacitor ( $C_{di}$ ) is a function of the electrode potential. The value of  $C_{di}$  depends on the location of the electrode potential with respect to

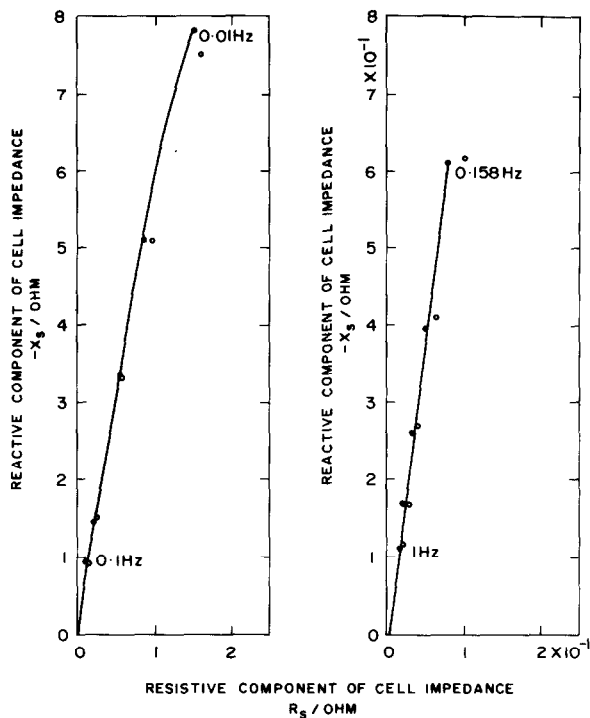


Fig. 2. Impedance spectrum of a 12 Ah nickel/cadmium cell at a cell voltage of 0.5 V (●). Calculated impedance spectrum from an equivalent circuit is also shown for comparison (○).

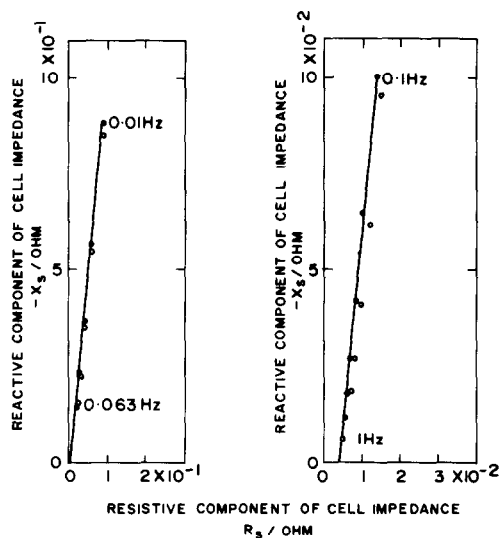


Fig. 3. Impedance spectrum of a 12 Ah nickel/cadmium cell at a cell voltage of 1.0 V (●). Calculated impedance spectrum from an equivalent circuit is also shown for comparison (○).

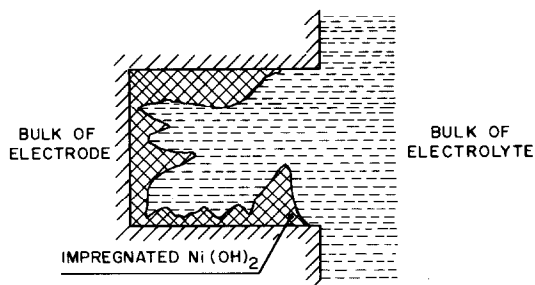


Fig. 4. Schematic view of the physical situation inside the pores of an impregnated nickel oxide electrode.

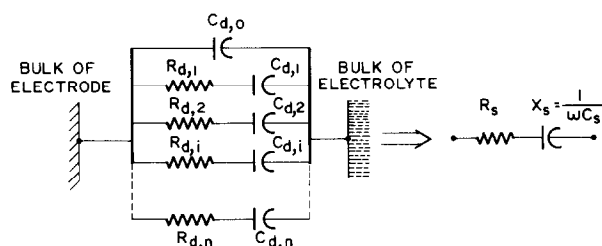


Fig. 5. Equivalent circuit representing the electrode/electrolyte interface of an impregnated nickel oxide electrode in the double-layer region.  $R_{d,1}$ ,  $R_{d,2}$ , etc. represent resistance due to the  $\text{Ni(OH)}_2$  layer and  $C_{d,1}$ ,  $C_{d,2}$ , etc., are the double-layer capacitances associated with them.  $C_{d,0}$  is the double-layer capacitance at the unimpregnated sinter area.

its potential of zero charge, PZC.  $C_{di}$  is a minimum around 0.5 V which is the PZC for nickel electrode versus a  $\text{Cd/Cd(OH)}_2$  reference and increases with the cell voltage on either side of the PZC [5].

The resistance ( $R_{di}$ ) associated with each of the elemental capacitors ( $C_{di}$ ) depends on the resistivity of the active material. The latter is a function of the concentration of  $\text{NiOOH}$ , i.e., the state-of-charge of the electrode. The concentration of  $\text{NiOOH}$  is related to the cell voltage ( $V^r$ ) by the Nernst equation. Thus,  $R_{di}$  is lowest at  $V^r = 1.3$  V and increases as 0.0 V is approached.

A total equivalent circuit should consist of an infinite set of resistor-capacitor combinations. In a practical situation, however, it may be reasonably accurate to represent the double-layer impedance by about three to five resistor-capacitor combinations, suitably selected to represent the observed behaviour over the frequency range of interest.

### Equivalent-circuit fit to the experimental results

At this stage, it is instructive to determine whether an equivalent circuit of the type shown in Fig. 5 can be fitted to the experimental results when reasonable values are taken for the circuit elements.

An equivalent circuit has thus been fitted (by trial and error using a computer) to the experimental results at  $V^r = 0.5$  and 1.0 V. Three resistors and four capacitors were used and had the values shown in Figs. 6 and 7. The experimental results and

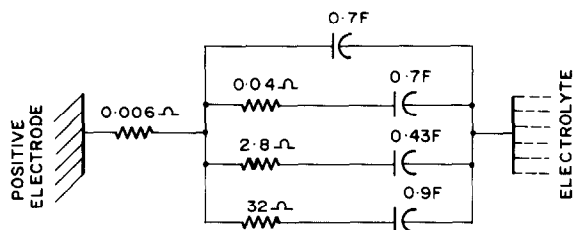


Fig. 6. Equivalent circuit that fits the experimental results at cell potential of 0.5 V, in the frequency range 1 to 0.01 Hz at 20 °C for a 12 Ah nickel/cadmium cell.

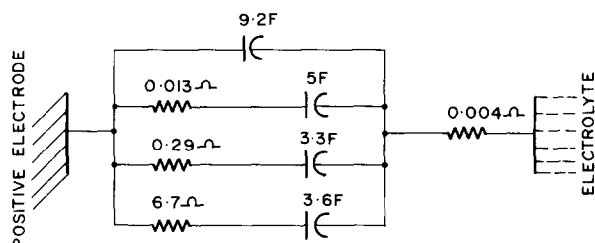


Fig. 7. Equivalent circuit that fits the experimental results at a cell voltage of 1.0 V in the frequency range 1 to 0.01 Hz at 20 °C for a 12 Ah nickel/cadmium cell.

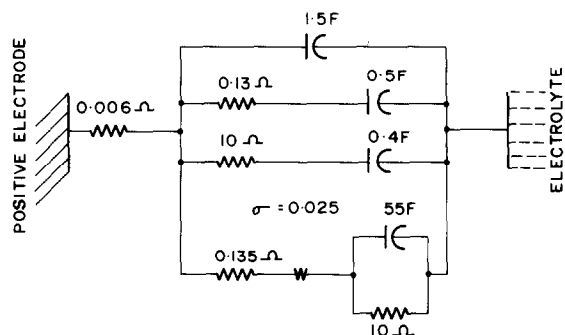


Fig. 8. Equivalent circuit that fits the experimental results at a cell voltage of 0.0 V in the frequency range 10 to 0.01 Hz at 20 °C for a 12 Ah nickel/cadmium cell.

the calculated fit based on the equivalent circuit are presented in Figs. 2 and 3 at  $V^r=0.5$  and 1.0 V, respectively. The calculated response closely fits the measured response in the frequency range 1–0.01 Hz. A comparison of Figs. 6 and 7 shows that  $R_{di}$  has larger values at  $V^r=0.5$  V than at  $V^r=1.0$  V. The values of  $C_{di}$  at  $V^r=0.5$  V are lower than at  $V^r=1.0$  V. Thus, the direction of the variation of  $R_{di}$  and  $C_{di}$  are as predicted by the theory discussed above.

The impedance of nickel/cadmium cells at a cell voltage of 0.0 V is due to the HER [4]. The double-layer impedance is in parallel to the impedance due to the HER. The double-layer impedance that fits the experimental results is shown in Fig. 8; it consists of two resistors and three capacitors together with the impedance due to the HER. It may be observed from Fig. 4 that the equivalent circuit fits the non-circular portion of the impedance spectrum fairly well.

## Conclusions

It has been shown that the double-layer impedance of a porous nickel oxide electrode is not affected by electrode porosity at low states-of-charge. Further, it can be modelled purely from physical considerations that explain the experimental spectrum fairly well. It is concluded that a porous nickel oxide electrode at low states-of-charge can be treated as a planar electrode with an area equal to its true area. The latter is covered with a layer of semiconducting nickel oxide with a thickness that varies greatly from place to place within the pore.

## Acknowledgements

The author is grateful to the Director of the ISRO Satellite Centre, Bangalore, for permission to publish this paper. Thanks are also due to Mr P. Ramachandran, Deputy Director, ESA; Mr B.L. Agrawal, Group Director, Power Systems Group; and Dr A. Subrahmanyam, Head, Chemical Battery Division for permission to perform this work. The author is also indebted to the late Professor S. Sathyanarayana for his valuable guidance.

## References

- 1 R. de Levie, in C.W. Tobias (ed.), *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 7, Wiley-Interscience, New York, pp. 326-329.
- 2 R. de Levie, *J. Electroanal. Chem.*, 261 (1989) 1-9.
- 3 S.U. Falk and A.J. Salkind, *Alkaline Storage Batteries*, Wiley, New York, 1969.
- 4 M.S. Suresh and S. Sathyanarayana, *J. Power Sources*, 37 (1992) 335-345.
- 5 D. Berndt, *Electrochim. Acta*, 10 (1965) 1067-1075.