

IMPEDANCE STUDIES OF NICKEL/CADMIUM AND NICKEL/HYDROGEN CELLS USING THE CELL CASE AS A REFERENCE ELECTRODE

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Summary

Impedance measurements have been made on several Ni/Cd and Ni/H₂ flightweight cells using the case as a reference electrode. For these measurements the voltage of the case with respect to the anode or cathode is unimportant provided that it remains stable during the measurement of the impedance. In the cells measured so far, the voltages of the cell cases with respect to the individual electrodes differ from cell to cell, even at the same overall cell voltage, but they remain stable with time. The measurements can thus be used to separate the cell impedance into the contributions of each electrode, allowing improved diagnosis of cell problems.

Introduction

Many impedance studies have been carried out on Ni electrodes and Ni/Cd and Ni/H₂ cells. Some studies have been made while the cells or electrodes were being discharged [1, 2], others at various open circuit voltages [3-6]. The impedances have been found to be strongly dependent on depths of discharge and/or voltage and on the procedure used to obtain the measurements. The studies have been similar qualitatively but not quantitatively.

In order for impedance to be used as a diagnostic tool for individual cells, more reproducible measurements must be obtained. It would also be desirable to be able to separate the contributions of the individual electrodes, especially for Ni/Cd cells. With Ni/H₂ cells one can almost always assume that any problems are due to the Ni electrode or separator and that the hydrogen electrode behaves reasonably reversibly. In this case the cell impedance is essentially that of the nickel electrode plus the ohmic contributions from the separator and electrolyte. However, with Ni/Cd cells, the Cd electrode can sometimes be the cause of poor cell performance, although it usually causes fewer problems than the Ni electrode. For a sealed cell with no reference electrode, there is currently no satisfactory way of determining

which electrode is behaving poorly without opening the cell and performing postmortem analyses.

This paper discusses preliminary measurements of impedance on flight-weight Ni/Cd and Ni/H₂ cells, using the case as a reference electrode in order to determine the impedances of each individual electrode. Although measurements so far have been limited, the method appears valid. We are reporting it at this time because of the urgent need for better diagnostic procedures for space-qualified Ni/Cd and Ni/H₂ cells.

Experimental

Impedance measurements were made using the Solartron 1250 Frequency Response Analyzer coupled with a Solartron 1286 Electrochemical Interface. Measurements were made on two flightweight 50 A h Ni/Cd cells from General Electric Corporation (now Gates), that had undergone acceptance testing several years ago, and which had subsequently been stored in the short-circuit condition. One was from a lot that had Cd electrodes which had been determined to be faulty from testing of other cells of the lot; the other was believed to have a good Cd electrode. At the time of testing, the cells had been stored for about six years. They were measured in the as-received condition, partially charged at 1 A for 5 h, discharged at 1 A to 0.1 V, where they were measured again. They were then charged at 5 A (*C*/10) for 16 h, discharged at 10 A (*C*/5) to 0.1 V and equilibrated at 1.275 V. The impedances were then measured at room temperature from 100 Hz to 0.0025 Hz with an RMS signal of 1 mV (peak to peak signal of 2.828 mV).

The Ni/H₂ cell studied was a 50 A h flightweight cell from Hughes which had completed acceptance tests and been cycled 900 real-time LEO cycles, followed by three years on open-circuit. The cell was charged to 1.275 V and equilibrated overnight. Impedance measurements were then taken of the total cell and the individual electrodes. The cell was then charged several times at *C*/10 for 18 h and discharged at *C*/2 to 1.00 V. Following this it was cycled at 60% DOD for three LEO cycles (55 min charge, 35 min discharge, 5% overcharge). Impedance measurements were taken again after equilibration of the cell at 1.275 V. The same parameters for the impedance measurements were used as with the Ni/Cd cells.

Results and discussion

A simplified circuit diagram for an electrochemical cell is shown in Fig. 1. A real cell usually has additional circuit elements including inductance due to the physical arrangement of the plates, modifications due to the porous nature of the electrodes, and adsorption capacitances and resistances. However, this simplified circuit diagram serves as a good first

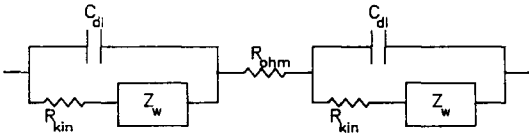


Fig. 1. Simplified circuit diagram for an electrochemical cell.

approximation. If the impedance of one of the electrodes is several orders of magnitude less than that of the other, as is usually the case with Ni/H₂ cells, one of the RC loops can be neglected, and the impedance of the cell can be treated as essentially that of the electrode with the higher impedance. The impedance data can be plotted in a number of different ways [7]. Bode plots (the log of the magnitude of the impedance *versus* the log of the frequency) are useful for comparing data that vary by orders of magnitude. Nyquist or complex plane plots (the real or in-phase component of the impedance *versus* the imaginary or out-of-phase component) are helpful in determining the ohmic and kinetic resistances and double-layer capacitances, and the slope of the Warburg plot (either the real or imaginary component *versus* the inverse square root of the angular frequency) gives information about the diffusion process (a large slope corresponds to slow diffusion). Figure 2 shows a typical Nyquist plot of a well-behaved Ni/H₂ cell at a voltage where the kinetic resistance is low. The impedance in this case is essentially that of the Ni electrode. The left intercept with the X-axis is the ohmic resistance, and the diameter of the semicircle gives the kinetic resistance. The right-hand portion of the curve is caused by slow diffusion processes. Similar plots are obtained with Ni/Cd cells [4 - 6], and the bulk of the impedance is also

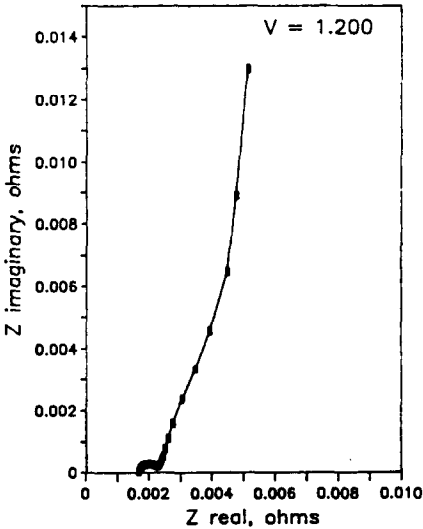


Fig. 2. Nyquist plot of impedance of typical 65 A h Ni/H₂ cell being tested for Space Station Freedom.

usually due to the Ni electrode. At low voltages, the diffusion portion of the curve may merge with the kinetic portion.

If the impedance of the cell varies from that of the typical cell, or if there is reason to suspect problems with the Cd or H₂ electrodes, it would be desirable to separate the impedance into the contributions from each individual electrode. This study was undertaken in order to see if the use of the cell case would enable such a separation.

In studying the impedances of cells containing Ni electrodes, the problem arises as to the best voltage or voltages for carrying out the measurements. It has been found that the impedances of Ni electrodes in the charged state (*i.e.*, at higher voltages) are very low and do not vary much from one electrode to another or from one manufacturer to another. However, at low voltages corresponding to almost completely discharged electrodes, impedances rise by several orders of magnitude. Figure 3 is the Bode diagram for the magnitude of the impedance *versus* frequency for a typical electrode, showing the changes with voltage as well as with the frequency. Figures 4 and 5 show how the kinetic resistance and the Warburg slope change abruptly by several orders of magnitude as the voltage is lowered. At very low voltages (cell voltages of less than 1.000 V or electrode voltages below about 0.050 V *versus* the Hg/HgO electrode) the impedances are very large, and there is a great deal of scatter. We have found that equilibrium cell voltages of 1.150 - 1.275 V (corresponding to voltages of the Ni electrode *versus* the Hg/HgO electrode of about 0.200 - 0.325 V) give sufficient differentiation of the impedances with less scatter than at lower voltages. The measurements reported below were taken at cell voltages of 1.275 V.

We have also found significant differences at low voltages between electrodes from different manufacturers, in addition to small differences between individual electrodes from the same manufacturer. This is not

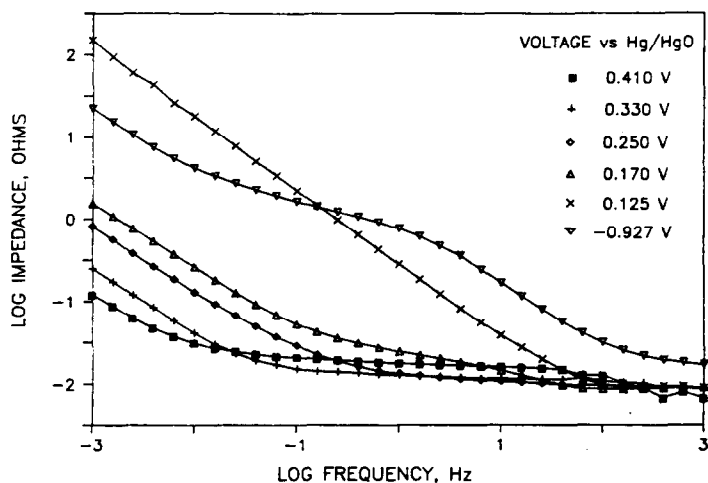


Fig. 3. Dependence of impedance on voltage for a Gates electrode, 42.9 cm², 31% KOH, after 12 cycles.

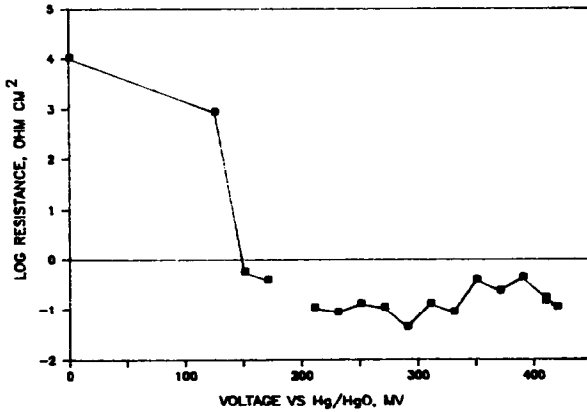


Fig. 4. Changes of kinetic resistance with voltage, Gates electrode, normalized.

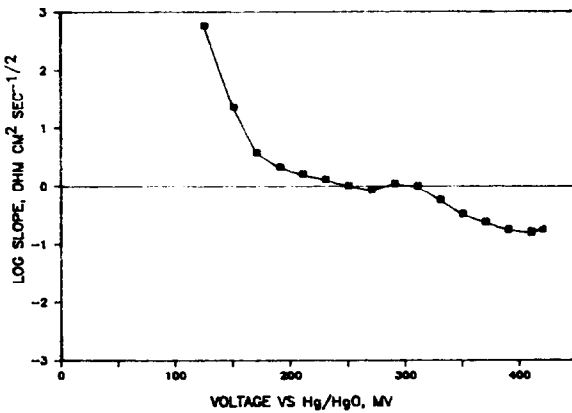


Fig. 5. Changes of Warburg slope with voltage, Gates electrode, normalized.

important if one is comparing cells from a single manufacturer, but must be taken into account if comparisons are made between electrodes or cells from different sources.

Recent studies in our laboratories have also indicated that measurements of impedances of the Ni electrode are more reproducible if the cells or electrodes are equilibrated at the voltage of interest. Equilibration times required vary from a few minutes for highly charged electrodes to several hours, or overnight, or longer, for electrodes at low voltages. The voltage range described above allows reasonable equilibration times of 15 min to several hours, depending on the electrode and the magnitude of the change from the initial voltage to the equilibrium voltage desired.

The voltage of the Cd electrode is reasonable stable, and it can be used as a reference electrode, although it is less satisfactory than the Hg/HgO electrode [8]. If the electrode is partially charged so that there is a reasonable amount of both metallic Cd and Cd(OH)₂ present, the potential should

be quite close to the theoretical value ($E^0 = 0.809$ V *versus* SHE). Thus, if the voltage of the cell case *versus* the Cd electrode is fairly constant, we can assume that the cell case voltage is not changing significantly.

The voltages of the cell cases with regard to the Cd and Ni electrodes at various times are given in Table 1. We see that the voltages of the case *versus* the Cd electrodes are quite stable, especially over short periods of time, while the voltage of the Ni electrode *versus* the case varies gradually with time. Although it is only necessary that the case voltage remain constant during the impedance measurement, it is interesting to speculate as to what electrode reaction is determining the potential of the case. The standard voltages of several possible couples are presented in Fig. 6, along with the couples for the Ni and Cd electrode reactions, the Hg/HgO reference electrode, and the case voltages for the two Ni/Cd cells studied.

TABLE 1

Voltages of cases of Ni/Cd cells *vs.* individual electrodes

	At time of impedance	Overnight stand	After recharge	Two months OCV
Cell L13-012				
Cell voltage	1.275	1.181	1.275	0.243
Case <i>vs.</i> Cd	0.350	0.350	0.349	0.318
Ni <i>vs.</i> case	0.925	0.831	0.926	-0.076
Cell L07-275				
Cell voltage	1.275			0.413
Case <i>vs.</i> Cd	0.648			0.631
Ni <i>vs.</i> case	0.627			-0.218

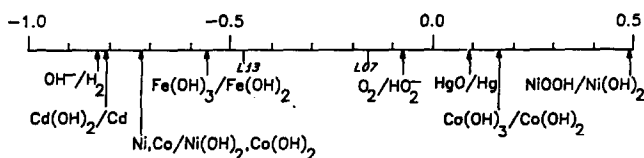


Fig. 6. Standard reduction potentials in basic solution and potentials of cell cases for Ni/Cd cells L07 and L13.

Flightweight Ni/Cd cells have stainless steel cases. If we compare the data in Table 1 with the values in Fig. 6, we see that the potential of the case with respect to Cd for cell L13-012 is somewhat higher than that of the $\text{Fe}(\text{OH})_3/\text{Fe}(\text{OH})_2$ potential; that of the other cell is not close to that of any obvious couple. There are no other metal/metal oxide potentials in this voltage range that could reasonably be considered as the source of this potential. Thus the potential-determining reaction cannot be determined at this time, but since the potential is stable for a reasonable time period, determination of the impedance using the case as the reference is feasible. The

potential may be a mixed potential or it may be affected by organic components from degradation of the separator.

Impedance measurements were made on the complete cell and on each of the electrodes individually, using the case as a reference. Figure 7 shows the arrangement of the leads for each measurement. The voltage between the two reference electrodes was maintained constant during the measurement. The experiments were interrupted several times during the course of the measurements of the individual electrode impedances to see if the cell voltage, and the voltage of the electrode which was not being measured, had changed. If the cell voltage had fallen (in no case was this more than 3 - 4 mV), the cell was again brought to the initial voltage before the measurements were continued.

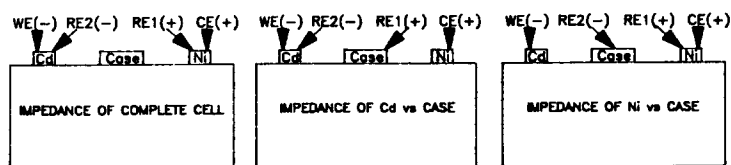


Fig. 7. Arrangement of leads for impedance measurements.

The results are plotted either as Bode plots or Nyquist plots. The Nyquist measurements were corrected for ohmic resistance, since it was not known initially whether the sum of the ohmic resistances between the case and the individual electrodes would equal the ohmic resistance between the two electrodes. (The results of the measurements subsequently showed that this was unnecessary; each of the resistances between the case and the individual electrodes was half of the ohmic resistance of the complete cell.) The corrected impedance for the two electrodes was added together at each frequency to give a calculated impedance for the complete cell. This calculated impedance was then compared with the experimental impedance for the cell (which had also been corrected for ohmic resistance). The values were essentially the same except at low frequencies where the impedances are higher and the scatter greater, indicating that the method is valid.

Figure 8(a) is the Nyquist plot for the impedances in cell L13-012, the cell which was presumed to have a poor Cd electrode. It can be seen that the sum of the impedances for the individual electrodes at each frequency is equal to the measured impedances for the total cell. The same behavior is shown in Fig. 8(b) for cell L07-220, from a lot with "good" Cd electrodes.

Figure 9(a) compares the impedances of the "good" and "bad" Cd electrodes using the Bode representation. The impedance of the "bad" Cd electrode in cell L13-012 is higher at low frequencies (diffusion controlled region) by half an order of magnitude. Figure 9(b) is the comparable plot for the Ni electrodes. In this case the low frequency impedance of the Ni electrode in cell L13-012 is lower than that in cell L07-220. The Nyquist plots are shown in Fig. 10.

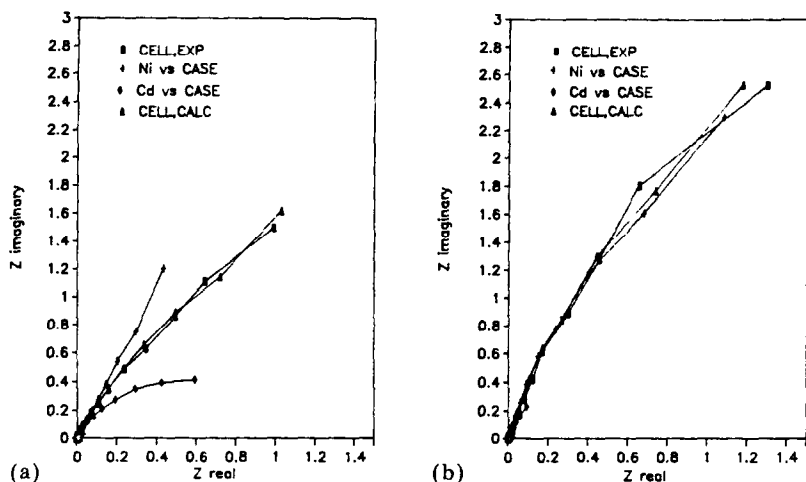


Fig. 8. Comparison of sums of individual electrode impedances of Ni/Cd cells with experimental cell impedances, Nyquist plot. Cell voltage = 1.275 V. (a) Cell L13; (b) Cell L07. (Scale of axes is unequal in order to show data more clearly.)

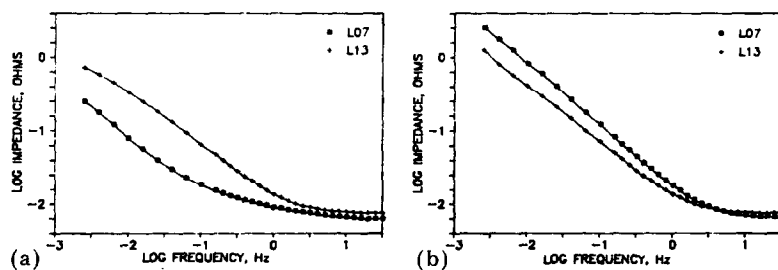


Fig. 9. Impedances of individual electrodes in cells L07 and L13, Bode plot. Cell voltage = 1.275 V. (a) Cd electrodes; (b) Ni electrodes.

The values of the kinetic resistances, Warburg slopes, and electrode capacitances that can be obtained by analysis of the data, using the circuit diagram for an individual electrode, are not reported, since we believe that the cells had not been cycled sufficiently after the open-circuit or short-circuited storage to obtain reproducible results. The data are presented primarily to describe the method and indicate its probable validity. However, we feel that the results are qualitatively correct.

The data for the Ni/H₂ cell after cycling are presented in Fig. 11. The Bode representation is used since the nickel electrode impedance and the hydrogen electrode impedance differ by about two orders of magnitude. The impedance parameters are given in Table 2.

In both sets of measurements of the Ni/H₂ cell the voltage of the cell case was not as stable as with the Ni/Cd cells. Sometimes the voltage was close to the Ni potential, at other times close to the potential of the H₂ electrode. During the measurements of the impedance of the Ni electrode

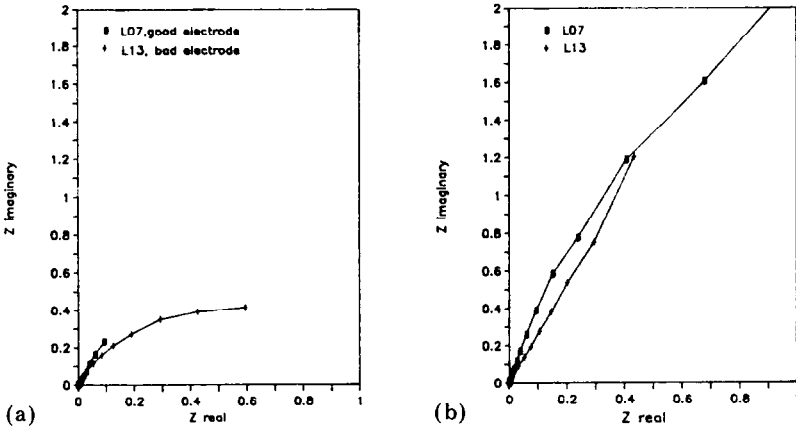


Fig. 10. Impedances of individual electrodes of cells L07 and L13, Nyquist plot. Cell voltage = 1.275 V. (a) Cd electrodes; (b) Ni electrodes. (Scale of axes is unequal in order to show data more clearly.)

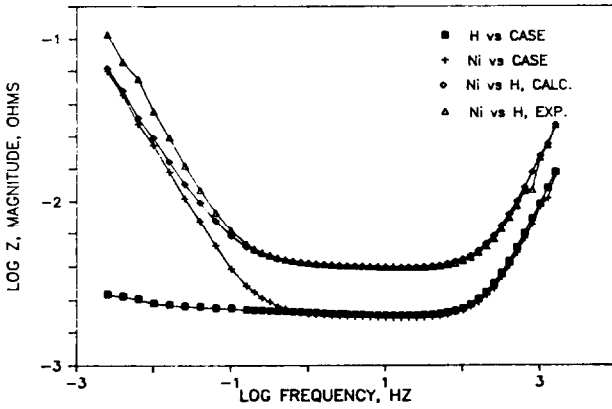


Fig. 11. Comparison of sums of individual electrode impedances in 50 A h Ni/H₂ cell with experimental cell impedance, Bode plot. Cell voltage = 1.275 V.

TABLE 2
Impedance parameters for Ni/H₂ 50 A h cell

	R_{ohm} ($m\Omega$)	R_{kin} ($m\Omega$)	Slope	Capacitance (Farads)
Complete cell	4.00	—	0.0063	—
Ni vs. case	1.96	—	0.0041	—
H vs. case	2.05	—	0.000056	—

the case potential remained stable, *i.e.*, the cell voltage after the measurement was essentially the same as before, and no appreciable d.c. current was noticed. However, during the measurement of the impedance of the

hydrogen electrode, the cell voltage changed by several hundred mV and a large d.c. current was noticed. We suspect that the instability of the case voltage may be due to the difference in the case material from that of the Ni/Cd cells. The case of the Ni/H₂ flightweight cell is made of Inconel, while that of the Ni/Cd cells is steel. The voltages of the case *versus* Ni in nine boilerplate Ni/H₂ cells housed in standard steel pressure vessels are in the same range as those of the two Ni/Cd cells described above and seem to be as stable as in the Ni/Cd cells. The difference is thus probably due to the case material rather than to the difference in the negative electrode or separator. Despite the changes in voltage of the case in the Ni/H₂ cell, the results are believed to be qualitatively correct.

Conclusions

Preliminary experiments indicate that the cell case can be used as a reference for Ni/Cd cells. The case can also probably be used as a reference for Ni/H₂ cells, although the potential of the case does not appear to be as stable as with the Ni/Cd cells. These measurements can be used to help determine which electrode is responsible for loss of performance. We are now cycling these Ni/Cd cells to determine changes in impedances of the individual electrodes with cycle life. We hope to make more measurements on a variety of Ni/Cd and Ni/H₂ cells from different lots to see if the cell and electrode impedances can be correlated with cycle life.

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