

# Impedance measurements on a spiral-wound nickel/metal hydride cell cycled in a simulated low earth orbit

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## Abstract

A spiral-wound size C cell was cycled at 25 °C in a low earth orbit regime (LEO) at 50% depth-of-discharge (DOD) with approximately 5% overcharge. The nominal capacity was 3.5 Ah. The cell was cycled for 2000 cycles. Capacity checks and impedance measurements over the complete range of state-of-charge were made upon receipt and after 500, 1000 and 2000 cycles. The capacity of the cell was essentially unchanged until after the impedance measurements at 2000 cycles. Only small changes in the impedance parameters were observed, but there was somewhat more scatter in the data after 2000 cycles. When the cell was returned to LEO cycling after 2000 cycles, only 38% of the capacity could be obtained. It is believed that the cell failed because of an equipment failure at the end of the final impedance measurements which allowed an overdischarge.

## Introduction

Nickel/metal hydride cells have been under intensive development in the last few years, and several manufacturers are selling these for both commercial markets [1, 2] and for space applications [3]. We are initiating testing of these for low-earth orbit applications. Since spiral-wound cells are readily available, we began with cycling and impedance measurements on an Ovonics size C cell with a nominal capacity of 3.5 Ah.

## Experimental

Short leads were soldered onto the two ends of the cell. The capacity was measured by charging at a  $C/10$  rate for 16 h and discharging at a  $C/4$  rate to a cutoff voltage of 1.0 V. The initial capacity was 3.38 Ah. A value of 3.4 Ah was used in the computer program that controlled the cycling. Open-circuit voltage decay measurements when the cell was new gave a loss of about 18% of capacity in 24 h and 26% in 48 h.

After the initial capacity check, the cell was charged and the impedances measured at various depths-of-discharge (DOD). Measurements were made on the fully charged cell and then at increments of 10% DOD until the cell was fully discharged. (Additional measurements were taken at 1, 3 and 5% DOD after 500 cycles.) A program developed by Dr Stephen Lipka of Florida Atlantic University, CYCLER, was used to automate the charging, discharging and impedance measurements. The program was written in

Pascal and run on a DOS 286 computer with a PAR 273 potentiostat and a Solartron 250 frequency response analyzer. A Hewlett-Packard 3455A digital voltmeter was used to monitor the cell voltage. The computer was programmed to cut off the charging and discharge currents if a limiting voltage was reached in order to prevent overdischarge and overcharge. The change of voltage with time on open circuit after discharge was used to determine when the cell had reached a quasi-equilibrium state.

The desired DOD was obtained by starting each measurement in the fully charged state and discharging to the calculated DOD at a 20% LEO rate (0.343C). Impedance measurements were taken at the quasi-equilibrium voltage described below. A true equilibrium voltage is never reached. After the discharge current is interrupted, the voltage rises abruptly, then more gradually, eventually falling due to self-discharge. We assume that the maximum voltage reached corresponds to a quasi-equilibrium state. The time that it takes to reach this maximum varies with the DOD. At low DOD the time is brief, and at high DOD it is very long, on the order of days before self-discharge is appreciable. In order for the computer to determine when quasi-equilibrium has been reached, a parameter,  $\delta$ , is defined as the rate of change of the voltage versus time. Ideally, quasi-equilibrium would be reached when  $\delta=0$ . However it is impractical to wait to take the impedance measurements until the voltage stops rising completely, especially at high DOD. Because of the different times required to reach quasi-equilibrium at different states of charge, the value of  $\delta$  is set for each DOD based on prior observation of the voltage-time curve. The value selected may also depend on the type of cell under study (and how long one is willing to wait before taking the measurement). The rate of change of voltage with time is calculated by the computer program, and when this falls below  $\delta$ , the impedance measurements are carried out at this quasi-equilibrium voltage. For the fully charged cell,  $\delta$  was set at 0.005 mV/min, and this was decreased as the DOD was increased. For 10% DOD,  $\delta$  was set at 0.001 mV/min, and at 50% DOD and below was 0.00022 mV/min. Typical equilibration times using these values were about 20 min for a fully charged cell, 1-2 h at 30% DOD, and 4-6 h below 50% DOD.

After each measurement the cell was recharged by adding the capacity withdrawn on the prior discharge plus an additional 10% of the capacity of the cell.

The capacity on receipt was 3.38 Ah. After the initial impedance measurements, the capacity had increased to 3.47 Ah. The cell was then cycled for 500 LEO cycles at 50% DOD using a 55-min charge time and a 35-min discharge time. Approximately 5% overcharge was used. This corresponds to a 0.573C charge rate and a 0.857C discharge rate. The cutoff voltage on discharge was 1.00 V. The capacity and impedance measurements were then repeated. Measurements were repeated again after 1000 cycles and 2000 cycles.

After the cell failed, it was opened in order to determine the area and thickness of the individual electrodes for comparison of the impedances with those of boilerplate nickel/hydrogen cells on a unit area basis. The nickel electrode was about 40 mils (1 mm) thick with an area of about 94 cm<sup>2</sup>. (The initial thickness was probably smaller.) The hydride electrode was about 15 mils (0.38 mm) thick with an area of about 113 cm<sup>2</sup>. Attempts to make further measurements with the hydride electrode were unsuccessful due to its disintegration when current was applied.

## Results

The capacity remained essentially constant, increasing slightly to 3.49 Ah before cell failure at the end of the impedance measurements at 2000 cycles.

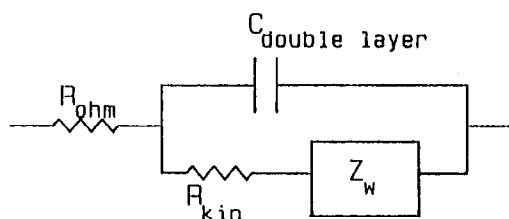


Fig. 1. Simplified circuit model for analysis of impedance parameters.

TABLE 1

Selected impedance parameters at 2000 cycles using the standard circuit model

DOD	$R_{ohm}$ (m $\Omega$ )	$R_{kin}$ (m $\Omega$ )	Capacitance (F)	Slope (m $\Omega$ s $^{-1/2}$ )
5	15.1	14.3	~ 2000	2.66
20	15.3	14.3	~ 4000	2.95
70	15.5	20.9	~ 6000	2.31
90	15.3	42.1	~ 8000	1.44

Initial analysis of the data was done using the conventional circuit shown in Fig. 1 with the ohmic resistance in series with a parallel combination of a capacitor representing the double-layer capacitance or adsorption capacitance and a resistor representing the kinetic resistance of the electrode. The ohmic resistance of the cell was about  $16.5 \pm 0.5$  m $\Omega$  and did not vary significantly with the DOD or cycle number. Little change in the other impedance parameter was observed until very low DOD, similar to observations on boilerplate nickel/hydrogen cells. Table 1 lists the parameters for the cells at 2000 cycles.

After 2000 cycles the impedances were essentially the same as at 1000 cycles, with slightly larger values at the lowest frequencies. At the higher states-of-charge there was an indication of the start of a second resistance-capacitance circuit. At the lower states-of-charge, there was slightly more scatter. Figures 2 to 5 show the comparisons for 5, 20, 70 and 90% DOD.

## Discussion

Very little data are available in the literature as yet on the impedances of hydride electrodes and nickel/metal hydride cells. Kuriyama *et al.* [4] measured impedances of electrodes made from an alloy powder ( $MmNi_{3.5}Co_{0.7}Al_{0.8}$ ) pressed with a polyperfluoroethylene/polyperfluoropropylene binder, both with and without a copper coating on the alloy particles. Agerwal *et al.* [5] measured impedances of a  $LaNi_5$  solid electrode. The electrodes in the Ovonic cell studied here are made from an alloy containing nickel, titanium, vanadium, zirconium and other trace elements.

In order to obtain an estimate of the impedance of the hydride electrode in this cell, the data were put on a unit area basis and the complex plane plots compared with those of the boilerplate nickel/hydrogen cells that we are also testing. This is shown in Fig. 6 for the two cells at a 20% DOD. The boilerplate nickel electrodes

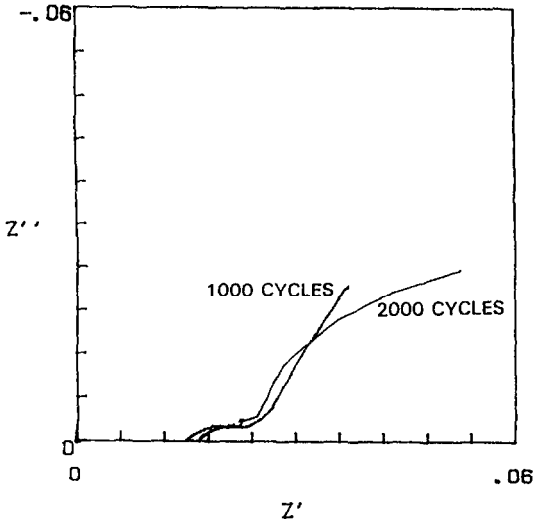


Fig. 2. Complex plane plots at 5% DOD for 1000 and 2000 cycles;  $V=1.395$ .

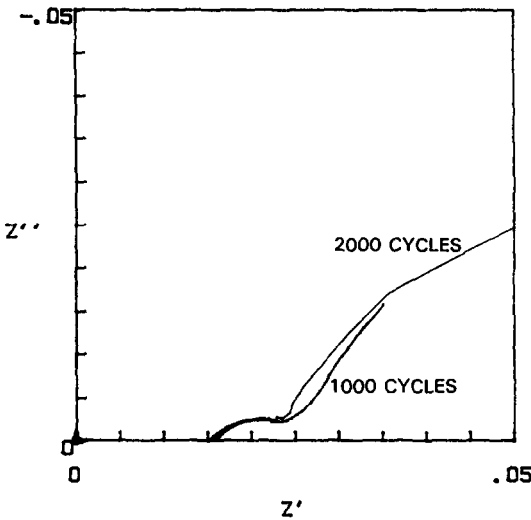


Fig. 3. Complex plane plots at 20% DOD for 1000 and 2000 cycles;  $V=1.340$ .

have capacities of about  $0.033 \text{ Ah/cm}^2$  compared with about  $0.037 \text{ Ah/cm}^2$  of the nickel electrodes in the metal hydride cell. If we assume that the impedance of the hydrogen electrode in the boilerplate nickel/hydrogen cells is negligible [6], and that the impedances of the two nickel electrodes are about the same at corresponding states-of-charge, then the increased impedance of the hydride cell over that of the boilerplate nickel/hydrogen cell can be attributed to the hydride electrode. An estimate of the impedance of the hydride electrode calculated from the differences at each frequency is shown in Fig. 7. Although these are very approximate calculations, they suggest that the

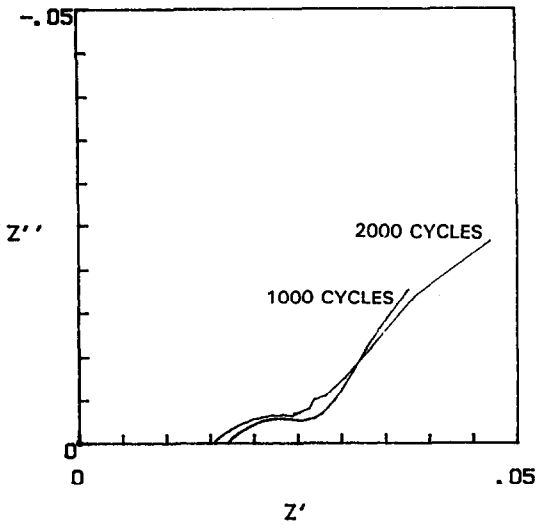


Fig. 4. Complex plane plots at 70% DOD for 1000 and 2000 cycles;  $V=1.262$ .

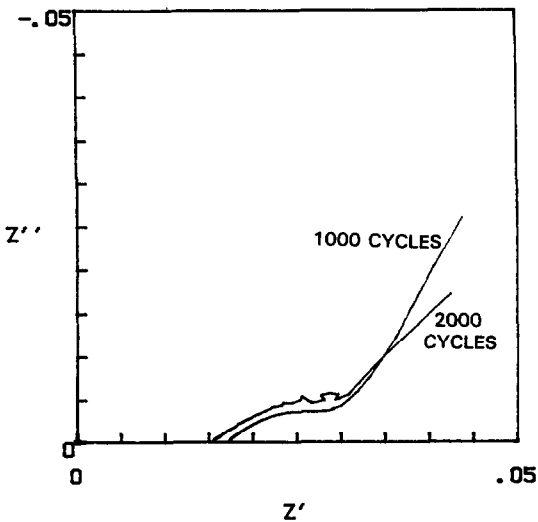


Fig. 5. Complex plane plots at 90% DOD for 1000 and 2000 cycles;  $V=1.206$ .

impedance of the metal hydride electrode is not negligible, in contrast to that of the gaseous hydrogen electrode in a typical nickel/hydrogen cell.

A confirmation that these estimated values for the impedance of the metal hydride electrode are reasonable can be obtained by comparison of these data with those of Agerwal *et al.* [5] (Fig. 8). The impedance data are of the same form as that found by these authors, (i.e., an ohmic resistance in series with a single parallel resistance-capacitance) circuit which includes a diffusion impedance) although they worked with a different alloy electrode ( $\text{LaNi}_5$ ) and used a solid rod rather than a powdered electrode. Estimating the true surface area of the powdered alloy from published

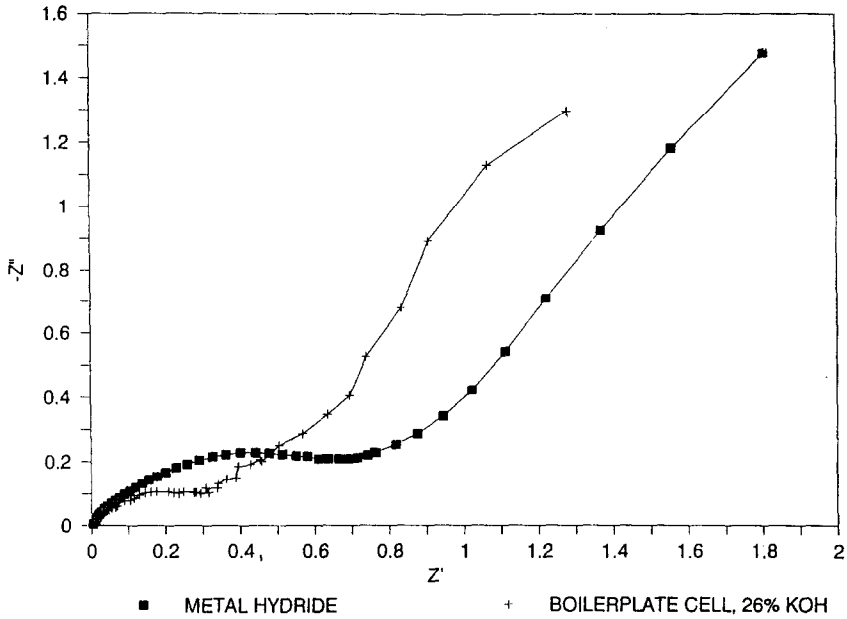


Fig. 6. Comparison of impedances of boilerplate nickel/hydrogen cell and nickel/metal hydride cell on a unit projected area basis, 20% DOD, and 1000 LEO cycles.

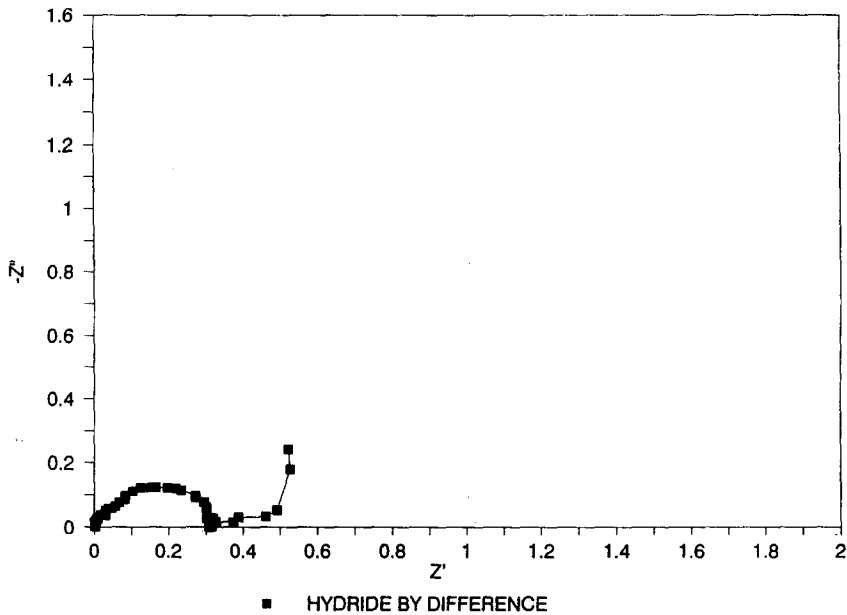


Fig. 7. Estimated impedance of the metal hydride electrode at 20% DOD by difference between nickel/metal hydride cell and boilerplate nickel/hydrogen cell, after 1000 LEO cycles.

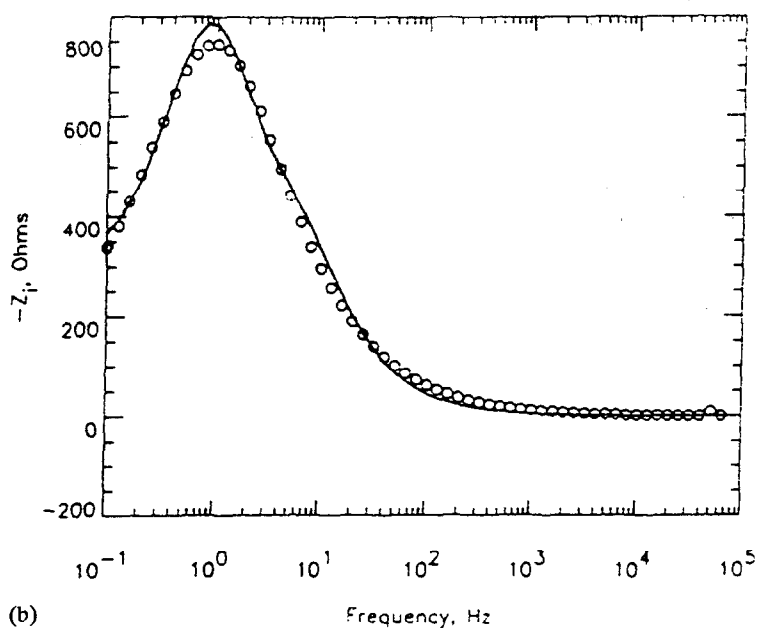
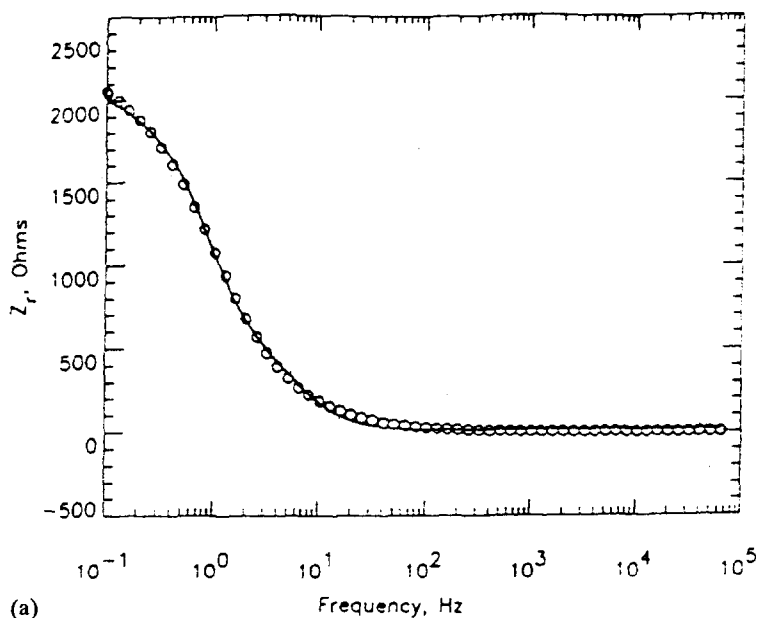
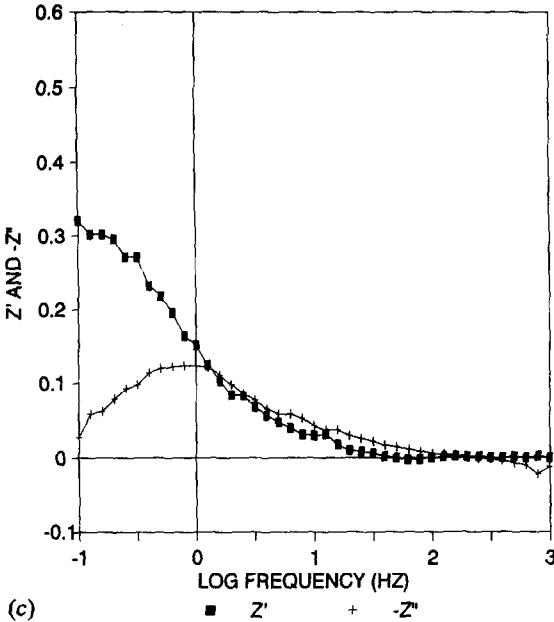


Fig. 8.

(continued)

literature data using a surface area of about  $2000 \text{ cm}^2/\text{g}$  and a capacity of about  $400 \text{ mAh/g}$  [6, 7], our impedances calculated with respect to the true surface area are of the same order of magnitude as those of Agerwal *et al.* [5], where the surface area was  $1.5 \text{ cm}^2$ .



(c) ■  $Z'$  +  $-Z''$

Fig. 8. Comparison of estimated impedance of metal hydride electrode at 20% DOD (estimated true surface area of about 20 000 cm<sup>2</sup>) with literature data of Agerwal *et al.* [5] for a partially charged electrode (1.5 cm<sup>2</sup> rod); (a), (b) Agerwal *et al.* [5], and (c) this study.

The data of Kuriyama *et al.* [4] were measured on a bonded hydride electrode with a binder of polyperfluoroethylene/polyperfluoropropylene (10 wt.%) and have an additional semicircle in the complex plane plots, believed to be due to the contact resistance between the alloy and the current collector. The remaining portion of the curve is similar to our curves, but insufficient data are given to make a more detailed comparison.

Spectroscopic analysis of the nickel electrode after dismantling showed a zirconium content of about 1%. This is consistent with the findings of earlier researchers that the zirconium dissolves extensively (and preferentially) from this alloy in 31% KOH at 70 °C [8]. Since nickel electrodes commonly last for thousands of cycles before failure, the failure is presumably caused by changes in the hydride electrode, either as a result of the cycling or from the failure of the equipment. It would be of interest to see if the metal ions that have precipitated in or on the nickel electrode have an effect on the cycle life, but this cannot be studied without measurements on the individual electrodes *in situ*.

More information about the changes brought about by cycling and the mechanism of failure might be obtained if both the nickel electrode and the hydride electrode are isolated from the case so that the case can be used as a quasi-reference electrode [6]. Studies will be initiated shortly on cells of this type which will allow the contributions of the individual electrodes to be determined.

Since the cell impedance did not change appreciably during the 2000 cycles that the cells were cycled, it cannot be determined from this limited study whether impedance can be used as a diagnostic criteria for metal hydride cells, especially in this situation where the negative electrode is connected to the case.



## Conclusions

Impedances of the spiral-wound metal hydride cell changed only slightly over the course of 2000 LEO cycles. Both the nickel electrode and the metal hydride electrode apparently contribute to the impedance of the cell, with the larger portion probably due to the nickel electrode. In the absence of a reference electrode, the contributions of each electrode to the impedance cannot be determined. Future measurements will be made with cells constructed with the hydride electrode not connected to the case. This arrangement allows the case to be used as a quasi-reference electrode, and thus the effects of cycling can be determined for the individual electrodes.

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