# IMPEDANCE MEASUREMENTS ON A SPIRAL-WOUND NICKEL/METAL HYDRIDE CELL CYCLED IN A SIMULATED LEO ORBIT

Margaret A. Reid
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, OH 44135

## 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 hours and discharging at a C/4 rate to a cut-off 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 hours and 26% in 48 hours.

After the initial capacity check, the cell was charged and the impedances measured at various depths of discharge. 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 depth of discharge was obtained by starting each measurement in the fully charged state and discharging to the calculated depth of discharge at a 20% LEO rate (0.343 C). 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 depth of discharge. At low depths of discharge the time is brief, and at high depths of discharge 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 vs 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 depths of discharge. 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 depth of discharge 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 minutes for a fully charged cell, 1-2 hours at 30% DOD, and 4-6 hours 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 minute charge time and a 35 minute discharge time. Approximately 5% overcharge was used. This corresponds to a 0.573 C charge rate and a 0.857 C 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 Ni/H$_2$ cells on a unit area basis. The nickel electrode was about 40 mils thick with an area of about 94 cm$^2$. (The initial thickness was probably smaller). The hydride electrode was about 15 mils thick with an area of about 113 cm$^2$. Attempts to make further measurements with the hydride electrode were unsuccessful due to its disintegration when current was applied.


EXPERIMENTAL 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.

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 ± 0.5 mOhms and did not vary with the DOD or cycle number. Little change in the other impedance parameters was observed until very low depths of

discharge, similar to observations on boilerplate Ni/H$_2$ cells. Table I 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 RC circuit. At the lower states of charge, there was slightly more scatter. Figures 2-5 show the comparisons for 5%, 20%, 70% and 90% DOD.

## DISCUSSION

Very little data is available in the literature as yet on the impedances of hydride electrodes and nickel-metal hydride cells. Kuriyama et al measured impedances of electrodes made from an alloy powder (MmNi$_{3.5}$Co$_{0.7}$Al$_{0.8}$) pressed with a PFE/PFP binder, both with and without a copper coating on the alloy particles. Agerwal and Orazem measured impedances of a LaNi$_5$ solid electrode. The electrodes in the Ovonics cell studied here are made from an alloy containing Ni, Ti, V, Zr 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 to those of the boilerplate Ni/H$_2$ cells that we are also testing. This is shown in Fig. 6 for the two cells at a 20% DOD. The boilerplate Ni electrodes have capacities of about 0.033 AH/cm$^2$ compared to about 0.037 AH/cm$^2$ of the Ni electrodes in the metal hydride cell. If we assume that the impedance of the hydrogen electrode in the boilerplate Ni/H$_2$ cells is negligible [8], 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 Ni/H$_2$ 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 Figure 7. Although these are very approximate calculations, they suggest that the impedance of the metal hydride electrode is not negligible, in contrast to that of the gaseous hydrogen electrode in a typical Ni/H$_2$ cell.

A confirmation that these estimated values for the impedance of the metal hydride electrode are reasonable can be obtained by comparison of this data with that of Agerwal and Orazem (Fig. 8). The impedance data are of the same form at that found by these authors, (i.e., an ohmic resistance in series with a single parallel RC circuit which includes a diffusion impedance) although they worked with a different alloy electrode (LaNi$_5$) and used a solid rod rather than a powdered electrode. Estimating the true surface area of the powdered alloy from published literature data using a surface area of about 2000 cm$^2$/g and a capacity of about 400 mAH/g [8], our impedances calculated with respect to the true surface area are of the same order of magnitude as those of Agerwal and Orazem, where the surface area was 1.5 cm$^2$.

The data of Kuriyama et al were measured on a bonded hydride electrode with a binder of polyperfluoroethylene/polyperfluoropropylene (10% by weight) 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 is given to make a more detailed comparison.

Spectroscopic analysis of the Ni electrode after dismantling showed a Zr content of about 1%. This is consistent with the findings of earlier researchers that the Zr dissolves extensively (and preferentially) from this alloy in 31% KOH at 70°[3]. 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 Ni 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 [8]. 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.

## CONCLUSION

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 Ni 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.

## REFERENCES

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Table I.—Selected impedance parameters at 2000 cycles using the standard circuit model.

| DOD | $R_{ohm}$, mOhm | $R_{kin}$, mOhm | Capacitance, Farads | Slope, mOhm sec$^{-1/2}$ |
|---|---|---|---|---|
| 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 |
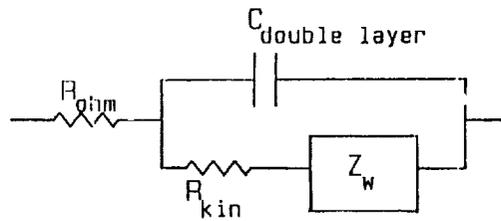
Figure 1.—Simplified circuit model for analysis of impedance parameters.
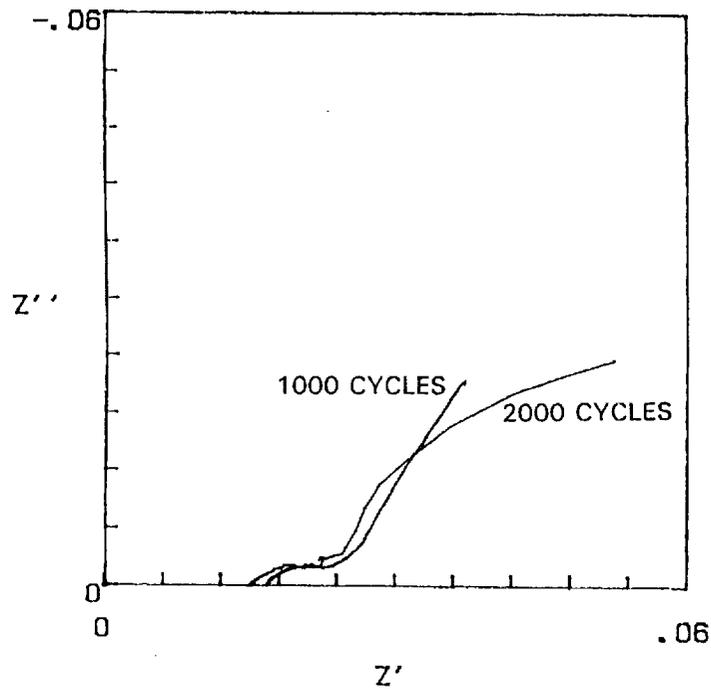


Figure 2.—Complex plane plots at 5 percent DOD for 1000 and 2000 cycles. V = 1.395.
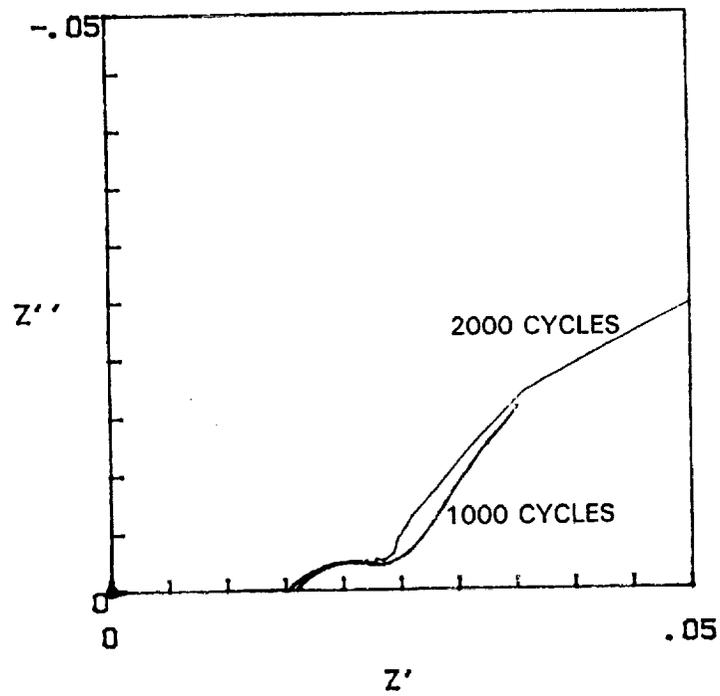
Figure 3.—Complex plane plots at 20 percent DOD for
1000 and 2000 cycles.  V = 1.340.
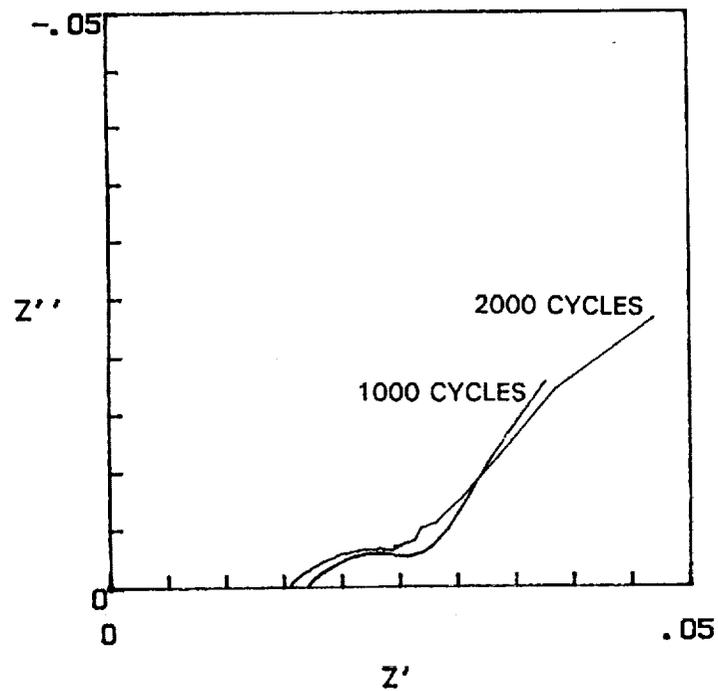


Figure 4.—Complex plane plots at 70 percent DOD for
1000 and 2000 cycles.  V = 1.262.

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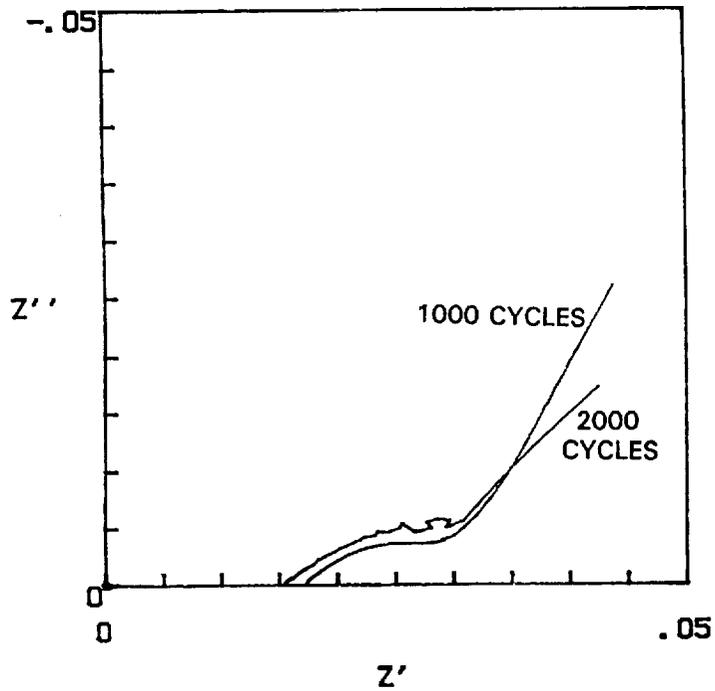
Figure 5.—Complex plane plots at 90 percent DOD for 1000 and 2000 cycles. V = 1.206.



METAL HYDRIDE    + BOILERPLATE CELL, 26% KOH
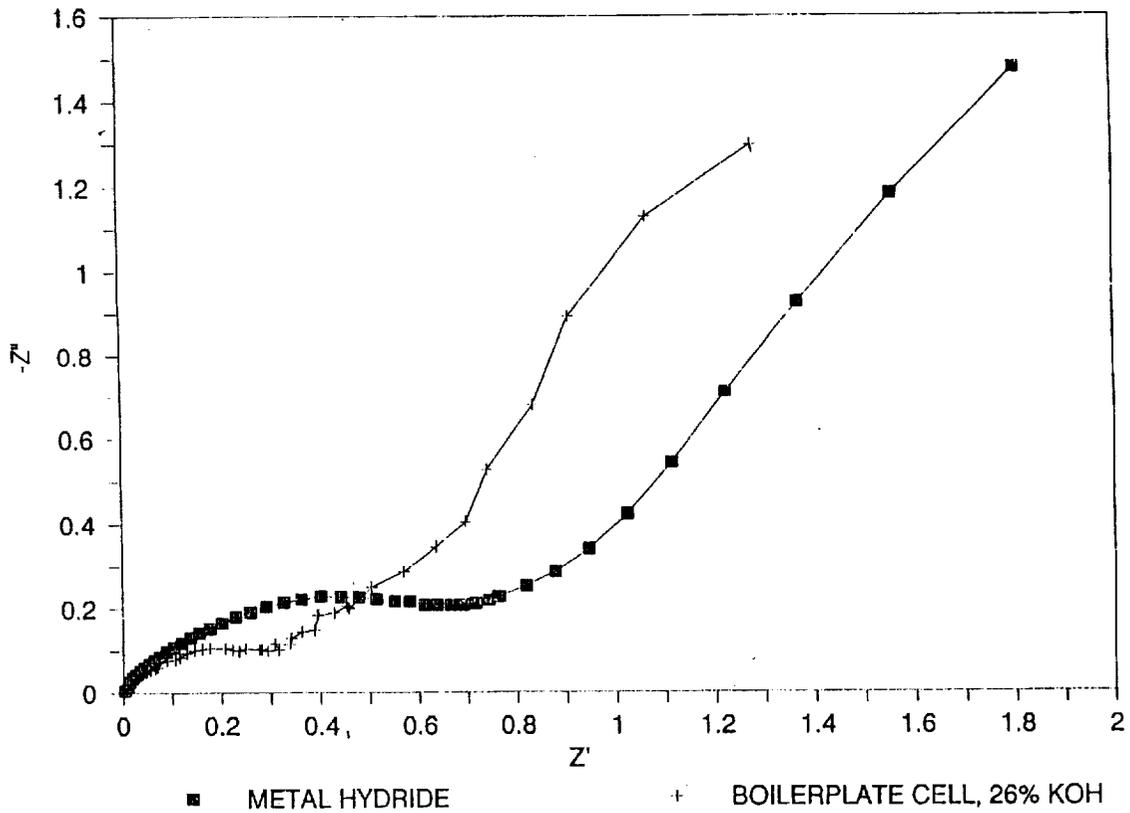
Figure 6.—Comparison of impedances of boilerplate $Ni/H_2$ cell and Ni/MH cell on a unit projected area basis. 20 percent DOD, 1000 LEO cycles.
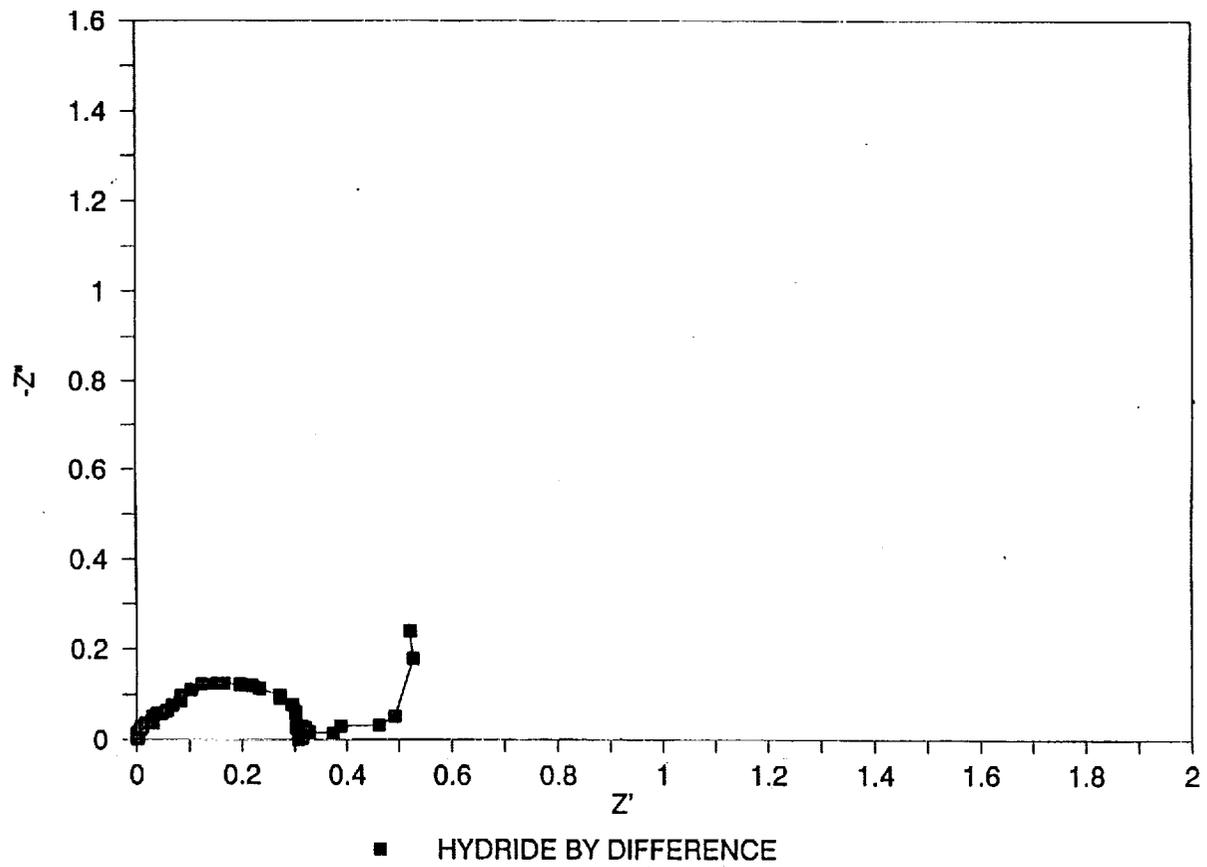
Figure 7.—Estimated impedance of the metal hydride electrode at 20 percent DOD by difference between Ni/MX cell and boilderplate Ni/H$_2$ cell. After 1000 LEO cycles.
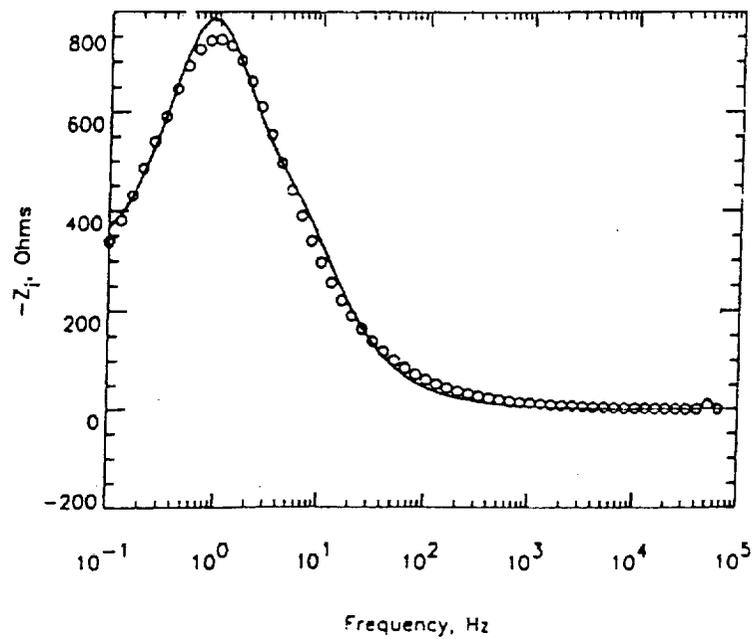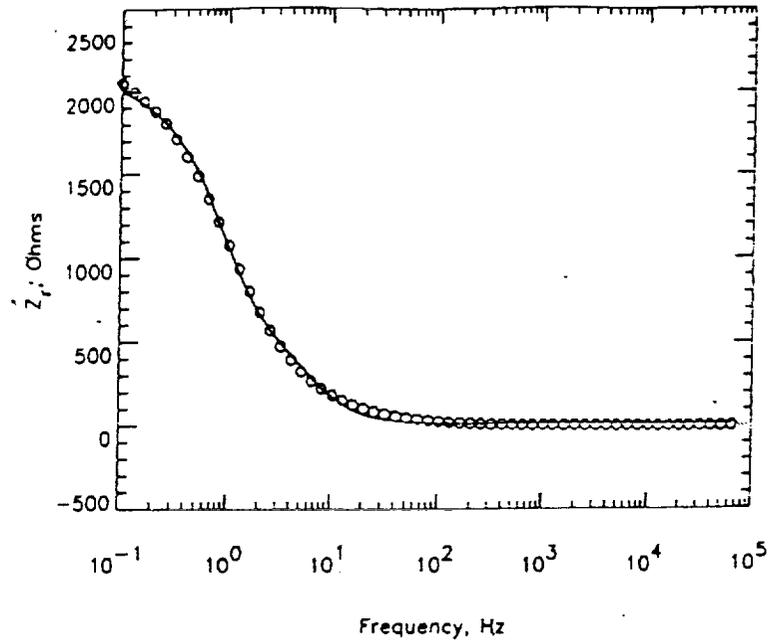
(a) Agerwal and Orazem.

Figure 8.—Comparison of estimated impedance of metal hydride electrode at 20 percent DOD (estimated true surface area of about 20 000 $cm^2$) with literature data of Agerwal and Orazem for a partially charged electrode (1.5 $cm^2$ rod).
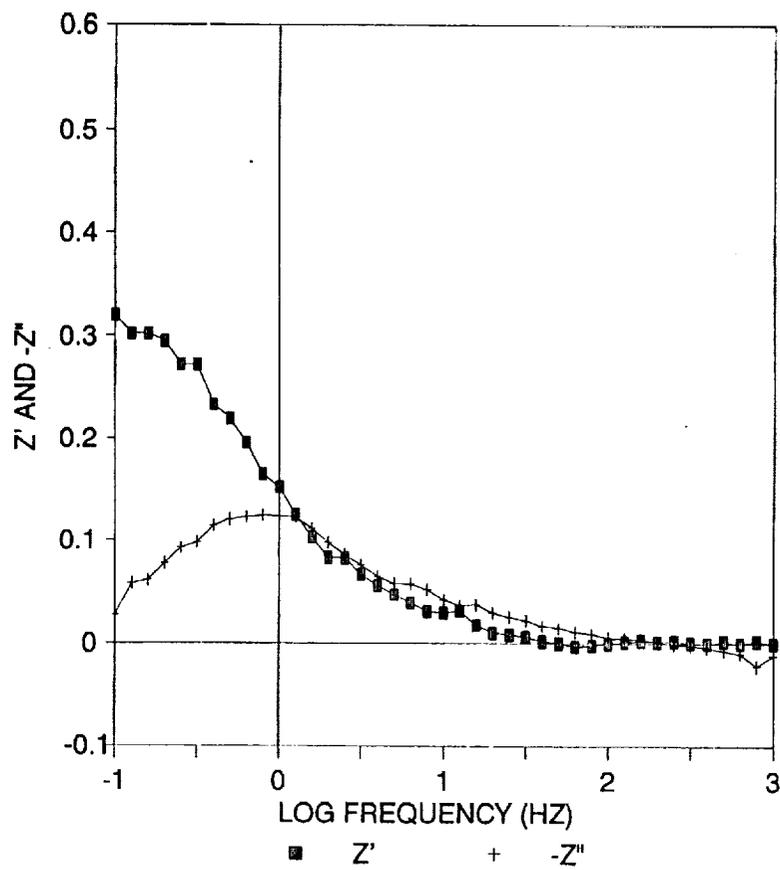
(b) This study.

Figure 8.—Concluded.