Changes in Impedance of Ni Electrodes Upon Standing and Cycling

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CHANGES IN IMPEDANCE OF NI ELECTRODES 
UPON STANDING AND CYCLING

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ABSTRACT

Impedances of Ni electrodes vary with many factors including voltage, cycling, and manufacturer. However, results from Ni/H₂ cells being tested for Space Station Freedom show that consistent results are obtained within a group of cells from the same manufacturer if the cells are cycled and stored in the same manner.

Impedance changes with storage and cycling are being investigated. Impedances are low in the fully charged state but rise abruptly by several orders of magnitude at a voltage corresponding to a very low state-of-charge. After standing for several months, this increase occurred at a higher voltage, consistent with an increase in structural order during storage which hinders diffusion of protons and reduces high rate capacity.

Early measurements on the effects of cycling on Ni/H₂ cells being tested for Space Station Freedom show differences between cells from different manufacturers.

INTRODUCTION

Impedances of Ni electrodes have been studied by many investigators (1-4). It has been found that the impedances increase by several orders of magnitude as the voltage decreases. Results from different investigators are similar qualitatively but not quantitatively. The question arises as to what conditions are required to obtain reproducible measurements. As part of our studies on Ni electrodes for space batteries, we have done measurements on a large group of electrodes from four different manufacturers and have found that the impedances of electrodes from any one manufacturer at a given voltage are reasonably reproducible, but there are major differences between manufacturers (5,6). We have been following the impedances of cells being cycled for Space Station Freedom and find the same results, that impedances of cells from a given manufacturer that have undergone the same conditions of storage and cycling have very similar impedances, but cells from different manufacturers have different impedance characteristics.
We have recently been examining the changes in impedance of electrodes that have been stored for up to a year. Since capacity losses are commonly observed upon storage, it is not surprising to find changes in impedance upon storage. In the present study we look at changes after standing for several months followed by two charge-discharge cycles. The nature of these changes are used to postulate a model for the discharge behavior that can explain the differences between new and stored electrodes and between electrodes from different manufacturers.

Impedances of cells being tested for Space Station Freedom are also being followed as a function of cycle life. These have been studied at only a few voltages due to the limited time available for investigation of these cells during life cycle testing. In order to obtain the maximum information from these measurements, the voltages chosen were selected so that they were in the range where the largest differences in impedance occur when the voltage is changed and where the largest differences are seen between electrodes from different manufacturers.

The impedances of two Ni/Cd cells have also been followed after short-circuited storage for five years followed by Low Earth Orbit (LEO) cycling.

EXPERIMENTAL

Impedances were measured using a Solartron 1250 Frequency Response Analyzer and either a PAR 273 Potentiostat or a Solartron 1286 Electrochemical Interface. This instrumentation measures impedance by analyzing a small AC signal which is superimposed on the desired DC voltage. The use of this technique, rather than the use of a current step during discharge, allows more precise control of the voltage at which measurements are taken, especially at the low voltages where the greatest changes in impedance and the largest differences between different electrodes are found. Measurements were made from 1585 or 1000 Hz to 0.0025 or 0.001 Hz (~6 decades).

All measurements were made after the cell or electrode had been fully charged, then discharged to the desired voltage. If multiple measurements were made, these were started at the highest voltage with subsequent measurements taken at progressively lower voltages.

Single electrode measurements were made with a 3.5 inch diameter electrode (42.9 cm²) manufactured for a Ni/H₂ flightweight cell. Electrodes were held at the measurement voltage for some time in order to reach a quasi-equilibrium state, in most cases until the current fell below 10 mA. A 1 mV RMS AC signal was then superimposed on the DC potential. Recent measurements were made using ZPLOT software (Scribner Associates, Charlottesville, VA) to control the instruments and plot the data.
The lightweight Ni/H₂ cells being tested at Lewis Research Center for Space Station Freedom are from three domestic manufacturers. Most of the cells are 65 AH capacity (a few are 50 AH cells) and have 3.5 inch diameter electrodes. Measurements were made at 1.200 or 1.275 V after equilibration at the measurement voltage until the DC current fell below 100 mA. In a few instances (due to the limited time available for measurements on these cells) the current was somewhat larger.

The choice of potentials for the cell measurements was made on the basis of earlier measurements with individual electrodes using a Hg/HgO reference electrode. At high voltages, (0.430 V to about 0.330 V), the impedances are low and there are negligible differences from one manufacturer to another but the differences become significant in the voltage range from 0.330 to 0.170 V. At lower voltages the impedances are higher but there are smaller differences between electrodes from different manufacturers. There is also much more scatter, and a much longer time is required to reach equilibration. Thus the voltage range from about 0.330 V to 0.170 V vs the Hg/HgO electrode is the region in which useful comparisons can be made.

Since there is no separate reference electrode in sealed cells, whether lightweight or boilerplate, the hydrogen electrode in Ni/H₂ cells and the Cd electrode in Ni/Cd cells must serve as the reference electrode in addition to acting as the counter electrode. In Ni/H₂ cells the impedance of the hydrogen electrode is almost always small compared to that of the nickel electrode so that use of the hydrogen electrode as reference is valid, and the impedance of the cell is essentially that of the nickel electrode (7). However, if we want to compare the results in Ni/H₂ cells to those for single electrodes measured against the Hg/HgO reference electrode, we must determine the relationship of the cell potential to the potential of the individual electrode against the Hg/HgO potential.

The potential of the Hg/HgO electrode vs the hydrogen electrode at 1 atm pressure will be +0.926 V in a solution of the same KOH concentration. However, in the Ni/H₂ cell the hydrogen pressure varies over the course of the charge-discharge cycle, and therefore the potential of the hydrogen electrode will vary. A typical hydrogen pressure for a new Ni/H₂ cell is about 50 PSIG (4.40 atm) in the discharged state. (The pressure is about 600 PSIG in the fully charged condition). Since we are working in the voltage range where the electrode is almost fully discharged, we can assume that the pressure is about 50 PSIG. (As the cells age, the hydrogen pressure increases, and correction must also be made for this). For a new cell the correction to the hydrogen electrode voltage and the cell voltage due to the increased hydrogen pressure is about 19 mV. Thus the voltage of the Hg/HgO electrode under these conditions is +0.945 V vs the H₂ electrode. Initial impedance measurements of the Ni/H₂ cells were taken at 1.275 V. This corresponds to a voltage of +0.330 V for the Ni electrode vs Hg/HgO, at the higher end of the voltage range of interest. However, it was found that measurements at lower voltages gave greater differences between cells from the different manufacturers and KOH.
concentrations, so subsequent measurements were made at 1.200 V. This corresponds to a voltage of +0.255 V for the Ni electrode vs Hg/HgO. Measurements at lower voltages than this required a longer equilibration time. The time schedule for cycling of these cells did not allow this.

In Ni/Cd cells the relationship of cell voltage to the voltage of the Hg/HgO electrode is slightly different than in the Ni/H₂ cell. The Hg/HgO electrode potential is +0.907 V vs the Cd electrode in a solution of the same KOH concentration (8), 38 mV lower than the H₂ electrode at 50 PSIG. Thus a Ni/Cd cell voltage of 1.200 V corresponds to a voltage of +0.293 V for the Ni electrode vs the Hg/HgO electrode. This is equivalent to a Ni/H₂ cell voltage of 1.238 V. A Ni/Cd cell voltage of 1.162 corresponds to a voltage of +0.255 for the Ni electrode vs Hg/HgO and thus is equivalent to a cell voltage of 1.200 V for a Ni/H₂ cell. (We are assuming that the Cd electrode contains excess Cd so that even at these low states-of-charge the equilibrium potential of the Cd electrode is close to that of a reversible Cd/Cd(OH)₂ electrode). The relationships between the cell voltages and the half-cell voltages used in the measurements are shown in Table I.

An additional complication in Ni/Cd cells is that the impedance of the Cd electrode is not always negligible, unlike the situation with the hydrogen electrode in the Ni/H₂ cells. In order to separate the total cell impedance into the contributions from the individual electrodes, the case can be used as a reference electrode (7). This has been shown to be valid since the voltage of the case is stable over the relatively short period of time required to make the impedance measurements. The voltage of the case is measured with respect to the individual electrodes at the cell voltage of interest (in this case 1.200 V), and this voltage is maintained between the case and the individual electrode during the impedance measurements. The impedances of the complete Ni/Cd cells using the Cd electrode as a reference and for the individual electrodes using the case as a reference will be given as functions of cycle life.

During an earlier study of loss of capacity as a function of manufacturer and storage conditions, impedances of electrodes from four companies had been measured at 0.200 V and 0.400 V after 10-12 cycles (5,6). The electrodes had been stored for a month under various conditions and recycled 10-12 times for capacity measurements. The impedance measurements were repeated at 0.200 V after the capacity determination and were quite close to the initial measurements. From this we conclude that 10-12 cycles is adequate under most conditions to bring the electrodes back to the initial impedance after short-term storage.

One of these electrodes (Gates Battery Corporation) was then used for more detailed measurements of impedance as a function of voltage (4). The measurements were then repeated after the electrode had been stored for four months at an OCV of about 0.200 V, charged, discharged and recharged again before measurements were taken. These measurements were repeated again after eight more months of storage.
Measurements on two flightweight Ni/Cd 50 AH cells were made after the cells had been stored short-circuited for about five years (7). The cells were then cycled under a LEO regime at 20% DOD. The impedances of the complete cells and of the individual electrodes using the cell case as a reference electrode were followed as a function of cycle life.

All complex plane and Bode plots presented here are the actual data taken from the individual cell or electrode but the parallel (or kinetic) resistances and Warburg slopes for the individual electrode have been normalized to a unit area basis.

Analysis of the impedance has so far been done using the simple circuit shown in Figure 1a. A typical complex plane plot for a Ni/H₂ cell is shown in Figure 1b, indicating that this circuit can serve as a good first approximation. The parameters obtained from the analyses are the ohmic resistance, parallel (kinetic) resistance, and the slope of the Warburg curve. For a planar electrode this slope is proportional to \( 1/CD^{1/2} \) where \( C \) is the concentration of diffusing species and \( D \) is the diffusion coefficient (9). For the porous electrodes studied here, this relationship is no longer followed exactly, but we can use the slope as a qualitative indication of the diffusion resistance. A higher slope signifies a slower rate of diffusion and a low slope a more rapid rate of diffusion.

RESULTS AND DISCUSSION

Table II shows data for measurements on cells from two manufacturers being tested for the Space Station after the initial acceptance testing. It can be seen that cells from each manufacturer give consistent results when measured at the same voltage. (Impedances of the cells upon receipt were much higher and there was a great deal of scatter, showing that a certain amount of cycling is required to bring the cells to a reproducible state, in agreement with widespread experience with Ni/H₂ and Ni/Cd cells). These results give us confidence in the reproducibility and validity of the measurements. It is not known whether the variations from cell to cell within each group are meaningful. The cells are now being life-tested under a LEO regime of 35% DOD with several percent overcharge, and the results of these tests will be analyzed to determine if these individual variations can be related to cycle life or whether they represent experimental uncertainty. In addition to demonstrating the reproducibility of results, these data also illustrate the differences between cells of different manufacture.

The impedance data for the new Gates electrode as a function of voltage are shown in Figs. 2 and 3. Bode plots are shown since the impedance changes by several orders of magnitude when the electrode goes from the fully charged to the short-circuited condition. The impedances are low at high voltages but rise sharply at low states-of-charge. An interesting feature is the decrease in impedance at very low voltages (illustrated by the curve at the short-circuited voltage of -0.926 V).
The reason for this is not clear. This phenomenon occurs at voltages below the potential at which Ni(OH)$_2$ can thermodynamically be reduced to Ni. This reaction is known to occur very slowly. If there is a layer of higher resistance material adjacent to the metal sinter, as has been proposed by some workers (10), it is possible that the reduction in impedance at very low voltages is due to reduction of this layer to Ni metal, or alternatively, to reduction of a small quantity of Ni ions to Ni atoms throughout the active material causing an increase in conductivity. It also may be related to the cobalt content of the active material (all the electrodes and cells studied contain cobalt additive). This interesting phenomenon is being explored further.

After the electrode was stored for four months, the experiment was repeated. The high voltage impedances were quite similar to the earlier values. However, as the voltage was lowered, the increase in impedance occurred at a much higher voltage than in the earlier measurements. Figures 4 and 5 show how the parallel (kinetic) resistances and Warburg slopes change with voltage for the two sets of measurements. The sharp rise in these parameters took place about 120 mV higher than in the earlier measurements. These changes occur within the same voltage range (0.330-0.170 V vs Hg/HgO) where we had previously observed differences in impedance between different manufacturers and with different KOH concentrations. Further storage of eight months produced only slight additional changes.

The measurements give support to proposals of earlier workers (1,11) that the discharge reaction is controlled by the solid state diffusion of protons through the active material. It can be seen that as the voltage is lowered, the parallel (or kinetic) resistance is low and fairly constant until equilibrium voltages are reached that correspond to very low states-of-charge. Up to this point there does not seem to be any significant potential dependence of the parallel resistance. If this resistance is limited by kinetic factors, one would expect a substantial change with voltage. The resistance then rises by over three orders of magnitude over a small potential range. The Warburg slope, which is a measure of the resistance to diffusion in the active material, rises at about the same voltage as the parallel resistance. This similar behavior, combined with the minimal changes in the parallel resistance with voltage until the transition voltage is reached, suggests that the discharge reaction is diffusion controlled rather than limited by a charge transfer process.

The changes in the impedance upon storage may also be related to increased resistance to proton diffusion. The active material is known to have a layered structure. Empirical formulas for battery-active materials include a substantial amount of water (12), and it is known that this is essential to the operation of the Ni(OH)$_2$ electrode. There are several theories as to how this is incorporated into the lattice. It has been proposed that the water is intercalated within the layers (13). A second theory which can also account for the empirical formulas observed is that there is a substantial fraction of vacancies in the Ni lattice.
Regardless of the nature of the included water, the increases in impedance produced by storage may be due to increased ordering within the active material upon standing so that diffusion of protons to the charge transfer sites is reduced. This could be caused by gradual rearrangement of the lattice which could either reduce the number of Ni vacancies within the lattice, or else increase the degree of stacking order within the layered structure leading to a reduction in the amount of interstitial water.

Electrodes that have been stored for long periods of time lose capacity and must be cycled a number of times to restore it. This fact, in conjunction with the changes in impedance with storage, suggests a possible model for the discharge process.

Let us consider a discharge at constant current at a moderately high rate. If we refer to Figures 4 and 5, at high voltages (high states-of-charge), the polarization will be small since the kinetic resistance and Warburg slope (the diffusion parameter) are low, and substantial current densities can be maintained.

As the electrode is initially discharged, the Warburg slope will gradually increase, and the diffusion polarization will likewise increase slowly. The slope will then increase more rapidly as the electrode becomes progressively discharged, and the diffusion polarization will increase more rapidly. The kinetic resistance does not increase appreciably until the point at which it rises abruptly, thus the kinetic polarization will be small up to this point. When the voltage reaches this point, the kinetic polarization will increase by several orders of magnitude, the voltage will fall below the usable range, and no more capacity can be withdrawn unless the discharge current is decreased. Thus the high rate capacity that can be withdrawn from a cell will be determined largely by the voltage at which the impedance parameters increase in magnitude and the magnitude of this increase.

Electrodes that have been stored for a long time are known to have a smaller high rate capacity than originally. We see that with stored electrodes the rise in Warburg slope and kinetic resistance occurs at a higher potential than before the storage. Thus the large increase in polarization takes place at a higher potential than for electrodes that have not been stored, and the available capacity will be less. Electrodes from different manufacturers will have differing high rate capabilities depending on the voltage at which the increase in parameters takes place and the magnitude of the changes in the parameters at this point. We plan to carry out more quantitative modeling of the discharge in terms of the impedance parameters.

Changes of impedance with cycling are also being studied, and measurements have been taken of the impedances of the cells undergoing test for the Space Station up to approximately 500 cycles. Again there are differences between cells from different manufacturers. Parameters are listed in Table III for cells from two companies. For the cells from
Parallel (kinetic) resistances and Warburg slopes for the two 50 AH Ni/Cd batteries that were stored for approximately 5 years are plotted in Figures 6-8. Since the impedances of these cells were not measured when new, no conclusions can be drawn about the effects of storage, but the data are included to show how the parameters change with cycling. The measurements were made at a cell voltage of 1.200 V which corresponds to a voltage of 0.293 V for the Ni electrode vs Hg/HgO. The initial impedance parameters seem to be high, by comparison with measurements on single electrodes from the same manufacturer. The parameters change very slowly with cycling. It can be seen that the Cd electrode impedance reaches a reasonably steady value after about 500 cycles but the impedances of the Ni electrode still seem to be decreasing after 1500 cycles, the latest point at which data have been taken. We plan to obtain some new Ni/Cd cells and measure their impedances as functions of voltage. Some will be cycled immediately and others will be cycled after storage for various lengths of time. The impedances will be followed as functions of cycle life. This will allow us to separate the effects of storage from the effects of cycling.

Analysis of the data using a more complex electrical circuit is under way. Further experiments to obtain a more complete data base are being carried out.

SUMMARY

The consistency of impedance measurements within each group of lightweight Ni/H₂ cells being tested for Space Station Freedom confirms that impedance measurements are reproducible provided that the same conditions of cycling and storage are maintained. However, electrodes and cells from different manufacturers vary widely, even with the same cycling and storage conditions.

Changes in impedance with storage were examined using a commercial Ni electrode. After the electrode was conditioned, measurements were made from the fully charged state to the short-circuited state. Kinetic resistances and Warburg coefficients rose abruptly by several orders of magnitude at about 0.20 V vs Hg/HgO. After standing for four months, measurements were repeated after cycling twice. The impedance parameters rose sharply at about 0.32 V, an increase of about 0.12 V. Further storage for eight months produced only slight additional changes. It is postulated that the changes are due to an increase in structural order during storage so that diffusion of protons through the active material is hindered. A model for the discharge reaction is postulated which could
account for the variations in capacity between new and stored electrodes
and for electrodes from different manufacturers.

Two Ni/Cd cells which were stored short-circuited for five years
were also examined. Impedance parameters fell slowly with cycling.

Early results from two types of cells being cycled for Space Station
show that there are substantial differences in how cells from different
manufacturers behave upon cycling. The impedances of these cells will be
followed as the life testing proceeds.

Impedance testing appears to be a very powerful method for study and
comparison of cells and electrodes, but any comparison must take into
account differences in cycling and storage history. The measurements can
aid in our understanding of the phenomena that take place on standing and
cycling and promise to be useful in modeling the discharge of Ni
electrodes.

REFERENCES

1) Zimmerman, M.R. Martinelli, M.C. Janecki, and C.C. Badcock, J.
2) R.T. Barton, M. Hughes, S.A.G.R. Karunathilaka, and N.A. Hampson, J.
4) M.A. Reid, Extended Abstracts of the 174th Electrochemical Society
5) M. Manzo, J. Power Sources, to be published.
7) M.A. Reid, J. Power Sources, to be published.
   1952.
9) A.J. Bard and L.R. Faulkner, Electrochemical Methods, Wiley, 1980,
   pp. 316 ff.

Table I. Voltages of Ni/H$_2$ Cells and Ni/Cd cells Corresponding to Various Half-cell Voltages.

<table>
<thead>
<tr>
<th>Ni vs Hg/HgO</th>
<th>COMPARABLE Ni/H$_2$ CELL VOLTAGE</th>
<th>COMPARABLE Ni/Cd CELL VOLTAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.200</td>
<td>1.145</td>
<td>1.107</td>
</tr>
<tr>
<td>0.255</td>
<td>1.200</td>
<td>1.162</td>
</tr>
<tr>
<td>0.293</td>
<td>1.238</td>
<td>1.200</td>
</tr>
<tr>
<td>0.330</td>
<td>1.275</td>
<td>1.237</td>
</tr>
</tbody>
</table>

Table II. Impedance Parameters of Ni/H$_2$ Cells from Two Manufacturers Being Tested for Space Station Freedom. Cell Voltage is 1.275 V. Measurements Taken after Acceptance Testing.

MANUFACTURER 1 (65 AH CELLS)

<table>
<thead>
<tr>
<th>CELL NUMBER</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
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<tbody>
<tr>
<td>R ohmic (mOhm)</td>
<td>1.61</td>
<td>1.28</td>
<td>1.07</td>
<td>1.13</td>
<td>1.63</td>
<td>1.13</td>
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<tr>
<td>R kin (mOhm)</td>
<td>1.4</td>
<td>1.3</td>
<td>1.5</td>
<td>1.7</td>
<td>1.7</td>
<td>2.2</td>
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<tr>
<td>Slope (mOhm sec$^{-1/2}$)</td>
<td>0.14</td>
<td>0.10</td>
<td>0.10</td>
<td>0.12</td>
<td>0.12</td>
<td>0.13</td>
</tr>
<tr>
<td>Capacitance (F)</td>
<td>27500</td>
<td>27000</td>
<td>27000</td>
<td>23000</td>
<td>25000</td>
<td>22000</td>
</tr>
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MANUFACTURER 2 (50 AH CELLS)

<table>
<thead>
<tr>
<th>CELL NUMBER</th>
<th>19</th>
<th>20</th>
<th>21</th>
<th>22</th>
<th>23</th>
<th>24</th>
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</thead>
<tbody>
<tr>
<td>R ohmic (mOhm)</td>
<td>1.15</td>
<td>1.06</td>
<td>1.50</td>
<td>1.52</td>
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<td></td>
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<tr>
<td>R kin (mOhm)</td>
<td>25</td>
<td>25</td>
<td>32</td>
<td>32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slope (mOhm sec$^{-1/2}$)</td>
<td>0.66</td>
<td>0.82</td>
<td>0.50</td>
<td>0.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capacitance (F)</td>
<td>30</td>
<td>20</td>
<td>30</td>
<td>35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Capacitances are derived from simplistic analysis of data. More sophisticated analyses are under way. These numbers are given for comparison between electrodes, as a figure-of-merit, and may not represent real capacitances.
Table III. Impedance Parameters of Two Lots of Ni/H₂ Cells Being Tested for Space Station Freedom after Acceptance Testing and after About 500 LEO Cycles at 35% DOD.

<table>
<thead>
<tr>
<th>MANUFACTURER 1, 1.275 V</th>
<th>AFTER ACCEPTANCE 500 CYCLES</th>
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</thead>
<tbody>
<tr>
<td>R ohmic (mOhm)</td>
<td>1.31</td>
</tr>
<tr>
<td>R kin (mOhm)</td>
<td>1.6</td>
</tr>
<tr>
<td>Slope, mOhm sec⁻¹/²</td>
<td>0.12</td>
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<tr>
<td></td>
<td>AVERAGE OF 6 CELLS</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>MANUFACTURER 2, 1.200 V</th>
<th>AFTER ACCEPTANCE 500 CYCLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>R ohmic (mOhm)</td>
<td>1.28</td>
</tr>
<tr>
<td>R kin (mOhm)</td>
<td>97</td>
</tr>
<tr>
<td>Slope, mOhm sec⁻¹/²</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>AVERAGE OF 5 CELLS</td>
</tr>
</tbody>
</table>
Fig. 1- a) Simplified circuit used for analysis of impedance data.
b) Complex plane plot of typical Ni/H₂ cell showing that this
circuit is a reasonable first approximation to the Ni electrode.

Fig. 2- Bode diagram, magnitude of impedance as function of voltage, Gates
electrode, 42.9 cm².
Fig. 6- Parallel resistances and Warburg slopes at 1.200 V for the 50 AH Ni/Cd batteries as functions of cycle life. Values are for the complete cell and are not normalized.

Fig. 7- Parallel resistances and Warburg slopes as functions of cycle life at 1.200 V cell voltage for Ni electrodes of the 50 AH Ni/Cd batteries. The case was used as the reference electrode.

Fig. 8- Parallel resistances and Warburg slopes as functions of cycle life at 1.200 V cell voltage for Cd electrodes of the 50 AH Ni/Cd batteries. The case was used as the reference electrode.
Changes in Impedance of Ni Electrodes Upon Standing and Cycling

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Impedances of Ni electrodes vary with many factors including voltage, cycling, and manufacturer. However, results from Ni/H₂ cells being tested for Space Station Freedom show that consistent results are obtained within a group of cells from the same manufacturer if the cells are cycled and stored in the same manner. Impedance changes with storage and cycling are being investigated. Impedances are low in the fully charged state but rise abruptly by several orders of magnitude at a voltage corresponding to a very low state-of-charge. After standing for several months, this increase occurred at a higher voltage, consistent with an increase in structural order during storage which hinders diffusion of protons and reduces high rate capacity. Early measurements on the effects of cycling on Ni/H₂ cells being tested for Space Station Freedom show differences between cells from different manufacturers.