

N95- 18985

1994

NASA/ASEE SUMMER FACULTY FELLOWSHIP PROGRAM

MARSHALL SPACE FLIGHT CENTER
THE UNIVERSITY OF ALABAMA

PROBING THE CHEMISTRY OF NICKEL / METAL HYDRIDE BATTERY CELLS
USING ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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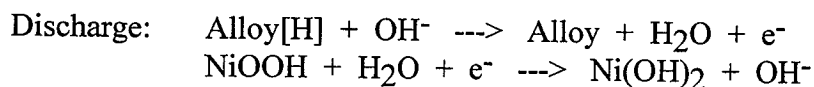
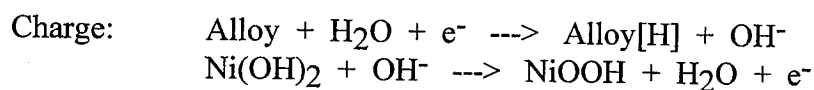
Electrochemical Impedance Spectroscopy (EIS) is a valuable tool for investigating the chemical and physical processes occurring at electrode surfaces. It offers information about electron transfer at interfaces, kinetics of reactions, and diffusion characteristics of the bulk phase between the electrodes. For battery cells, this technique offers another advantage in that it can be done without taking the battery apart. This non-destructive analysis technique can thus be used to gain a better understanding of the processes occurring within a battery cell. This also raises the possibility of improvements in battery design and identification or prediction of battery characteristics useful in industry and aerospace applications.

Impedance spectroscopy is an alternating current (ac) method, while battery cells are useful chiefly as a supply of direct current (dc). The ac signal is applied while the battery is held at a desired potential, and the signal perturbs the battery system slightly. The frequency of the ac signal is scanned to yield an ac frequency spectrum, normally ranging in this work from 10 kHz to 10 mHz, and often scanned to frequencies as low as 0.2 mHz. The highest frequencies generally give information about the fastest processes, such as electron transfer, charge transfer, and some chemical reactions. The lower frequencies result in data relating to the slower phenomena, such as diffusion parameters of the cell.

EIS as a technique is powerful and capable of yielding significant information about the cell, but it also requires that the many parameters under investigation can be resolved. This implies an understanding of the processes occurring in a battery cell. Many battery types were surveyed in this work, but the main emphasis was on nickel / metal hydride batteries.

Nickel / metal hydride battery cells are in the class of rechargeable cells along with nickel cadmium (NiCd) and nickel hydrogen (NiH₂) batteries. One electrode is NiOOH (which becomes Ni(OH)₂ in the discharged state), while the other is a metal alloy which is formed on a nickel substrate (at the charged state this forms a hydride, and at discharge the hydride is taken off). The first electrode is also used in other nickel cells, including the NiCd battery.

The chemical reactions of the cell during charging and discharging processes are:



One advantage of the Ni/MH cell over NiCd is an increase in the charge density, which results in more capacity for battery cells of the same mass. Various nickel-metal alloys are under consideration, each with somewhat different properties.¹

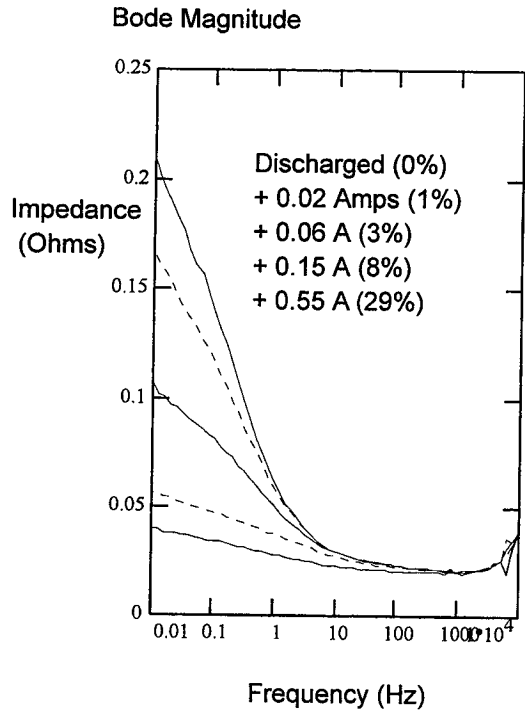
EIS is a method which probes all of the battery cell, not just a single area of interest, so one must have some general understanding of the processes occurring within the cell to be able to comprehend the results. Many of these processes are listed below:

- resistance at the metal-metal junctions within the leads and the electrodes;
- any effects related to a possible passivation layer on the NiOOH electrode;
- processes occurring at the interface of the electrode and the bulk phase (between the electrodes),
 - resistance due to electron transfer (e.g., electrons are given up by the hydride to the alloy in order to form the positive hydrogen ions),
 - resistance due to the chemical reaction (e.g., hydrogen ions reacting with hydroxide ions),
 - resistance associated with decreased availability of reactant (in the case of a limiting reactant),
 - capacitance associated with the double layer (a phenomenon occurring a few atom diameters away from the electrode surface caused by a response of the bulk phase to the charging of the electrode); and
- processes in the phase between the electrodes (referred to as the "bulk"),
 - resistance of the bulk (analogous to solution resistance in a typical electrochemical cell), and
 - impedance due to diffusion (this is known as the Warburg impedance).

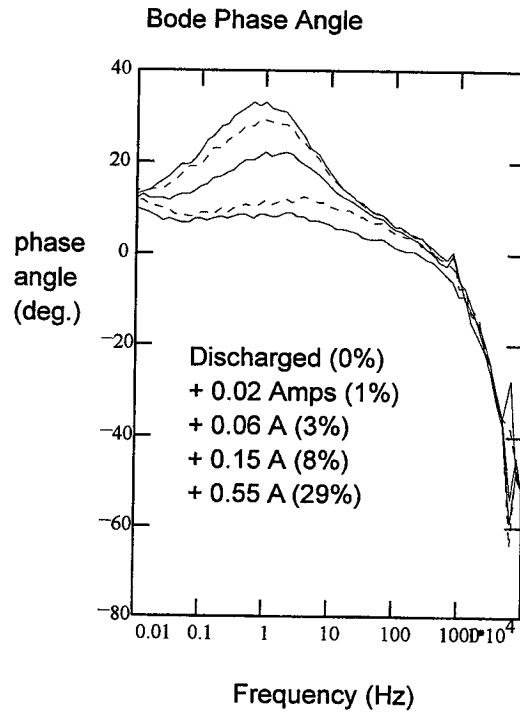
The large number of phenomena can result in a problem of resolving each interaction from the other, or may imply that many parameters are held constant and one or two of interest are investigated. To reach the goal of characterizing a battery cell with a model to show the contributions of each process, one would need to be able to either resolve each parameter (which is not possible) or have some control over a large number of these factors. This is a requirement which is beyond our capabilities at this time. We can, however, study the cell in a region in which we can resolve some of the chemical and physical phenomena, and gain some understanding of those processes.

The method employed in these experiments was to charge or discharge the battery cell to a desired level, allow the cell to equilibrate, and scan the impedance spectrum. It was noted that the impedance measurements varied considerably for the Ni/MH cell near the region of complete discharge. This region is presented in Figure 1. [An explanation of the graphical presentation of impedance spectra may be in order here. The plots included represent various forms of the information: one gives the magnitude of the impedance as a function of ac frequency; the second is a measure of the shift in the phase of the response when compared to the excitation frequency (known as the phase angle) as a function of ac frequency; and the third is a complex plane plot, presented with the real impedance -- the impedance in phase with the excitation -- on the x-axis, and the imaginary impedance -- the component out of phase with the excitation -- on the y-axis. The third plot (the complex plane plot) could also be presented as a three-dimensional figure, because the real and imaginary impedances are each a function of frequency. The result is that the highest frequencies yield points near the lower left of the graph and the lower frequencies appear at the upper right.]

A.



B.



C.

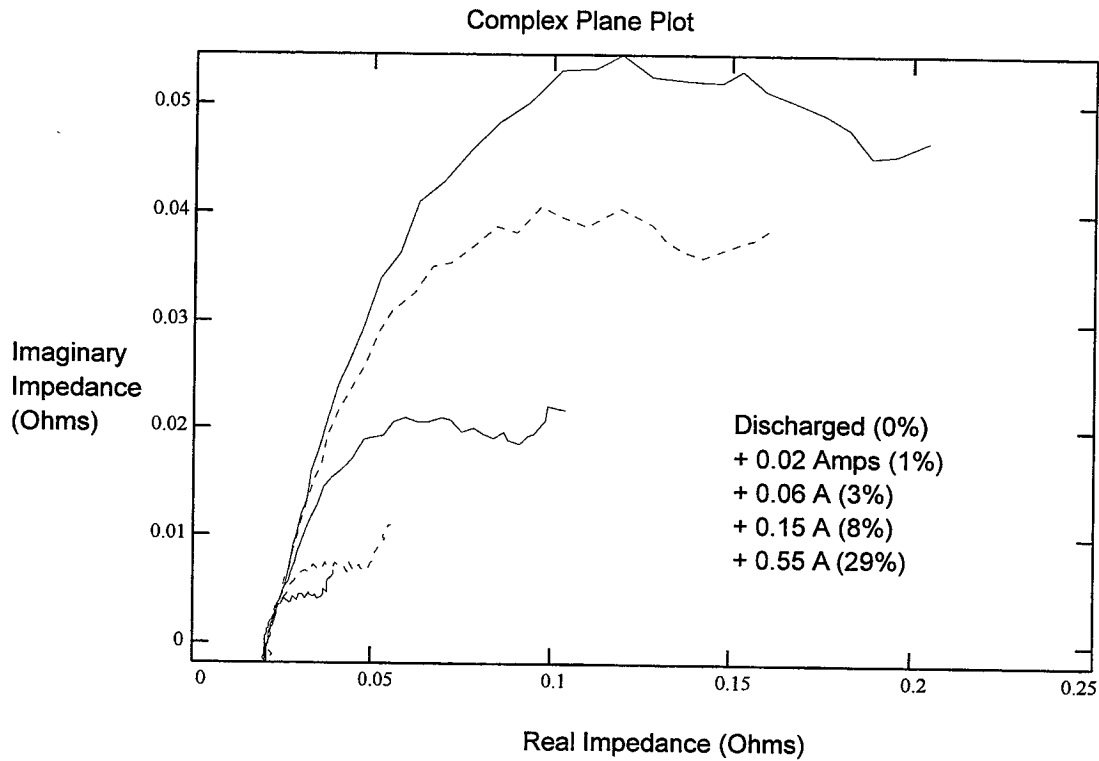


Figure 1. Ni/MH cells near full discharge. A) Bode Magnitude plot of total impedance. B) Bode Angle plot. C) Complex Plane plot; imaginary impedance versus real impedance.

The figures show a significant change in the impedance spectra as the cell approaches complete discharge. The capacity of the cell studied was 1.88 Amp-hours, and the percent charge is given in parentheses with each figure (legends correlate top-to-bottom with the various curves).

From the data shown, one can obtain information about the various resistance and capacitance processes for the cell. An equivalent circuit model is required, and one must choose a model which is appropriate. These vary considerably, ranging from simple models which do not even separate the contributions at separate electrodes, to those which model each conceivable contribution. Because of our efforts to look at only one type of change at a time, we chose the most simple model, deducing the responsible chemical or physical parameter from there. This model is given below in Figure 2. R_u is the uncompensated bulk resistance (including any ohmic resistance contribution from the electrode connections), C_{dl} is the capacitance of the double layer, R_{ct} is the charge transfer resistance (includes any resistance at the interface of electrode and bulk), and Z_W is the Warburg impedance (diffusion-related).

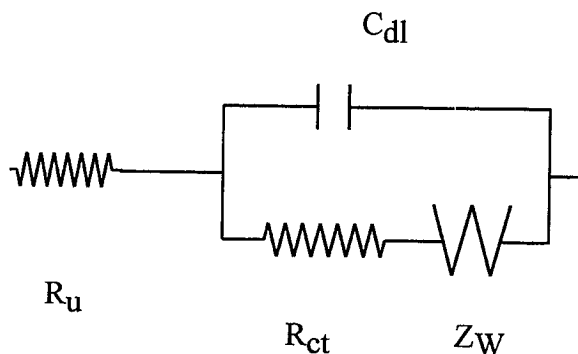


Figure 2. Circuit model used to determine chemical and physical parameters.

Analysis of the data show that the only significant trend is in the charge transfer resistance, R_{ct} . These data are given in Table 1, and the resistance values are graphed in Figure 2. The phenomena included in R_{ct} are electron transfer from the hydride to the electrode, charge transfer from the electrode to the hydroxide, and chemical reaction of hydrogen ion and hydroxide ion. Of these phenomena, the only one that actually is different near the discharge end must be the chemical reaction, analogous to a limiting reactant in chemistry. If the surface hydride is being depleted as the cell discharges, this would present a resistance to the cell, shown in the charge-transfer resistance. This effect is clear in the data presented by a previous author, but it is not discussed nor is any indication of its cause given.²

A second phenomenon observed was the change in impedance spectrum as the cell was cycled. A new battery cell yields different impedance spectra than a cell which has undergone charge and discharge cycles. The appearance of the spectra is similar, but they are offset by a factor. The resulting values of R_u , R_{ct} , and C_{dl} show the same trend in the charge-transfer resistance, but also show that the ohmic resistance, R_u , is changed. This value decreases as the

cell is moved through these "wake-up" cycles. The average value of R_{Ω} for new cells (not previously cycled) is approximately 0.13 ohms, while the resistance drops to 0.02 ohms for a cell which has been cycled. This could be due to several phenomena, including a change in the porosity of the electrode surface, a decrease in some passivation layer, or other processes unknown to us.

CHANGES NEAR COMPLETE DISCHARGE

Charge (Amp-hrs)	Cell Potential (Volts)	Capacitance (Farads)	Warburg Impedance (slope)	Resistance -- ohmic (Ohms)	Resistance -- chrg trnsfr (Ohms)
0.000	1.206	6.27	0.73	0.0215	0.1750
0.020	1.225	5.22	1.26	0.0218	0.1330
0.060	1.254	5.54	1.03	0.0215	0.0768
0.147	1.290	4.36	0.67	0.0207	0.0290
0.551	1.349	7.29	0.70	0.0202	0.0136
1.172	1.389	9.31	0.81	0.0202	0.0107
1.773	1.420	10.10	1.06	0.0204	0.0125

Table 1

This work shows that some chemical and physical parameters can be determined by the use of EIS. It is also clear, however, that more control of the chemical and physical processes is needed and that components of various composition are needed to separately determine the influence of changes in these processes and components. Others who have attempted to model such cells through the use of components with varying composition, have had some success, but have limited themselves to studies of single electrodes which are not part of working cells.³

This EIS technique is powerful in resolving the chemical and physical processes at work in an electrochemical system, but is likely to be limited to systems with a relatively small number of such processes.

¹Gates Aerospace Industries, "Nickel Metal Hydride Battery Product Information", 1992.

²M. A. Reid, *Electrochimica Acta*, **38**(14), 2037-2041.

³N. Kuriyama, T. Sakai, H. Miyamura, I. Uehara, H. Ishikawa, and T. Iwasaki, *J. Electrochem. Soc.*, **139** (7), L72-L73.