ADDITIONAL REVERSAL CHARACTERISTICS OF SEALED NICKEL CADMIUM CELLS

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TRW

To change the topic slightly, additional remarks on reversal characteristics of sealed nickel-cadmium cells. I gave a paper on reversal characteristics of nickel-cadmium cells 2 years ago, and those were state of the art cells.

We have done some further testing on state-of-the-art cells, and we have done some design work to improve the cells from the standpoint of hydrogen-nickel combinations.

(Figure 4-63)

This is a background on nickel-cadmium reversal characteristics. Nickel-cadmium cells are positive limiting on discharge, and when they are completely discharged, hydrogen is evolved from the positive electrode. One ampere-hour of overdischarge in reversal can generate enough hydrogen to increase the cell pressure of an average size cell, a 20-to 50-ampere hour cell, by 120 psi.

On an ampere-hour basis, the theoretical hydrogen evolution is quite extensive. But it can be kept at a minimum and even at zero by selection of a low reversal rate. Constant current reversals on state-of-the-art aerospace nickel-cadmium cells have shown that a steady-state condition, a concentration condition exists at C/100, around that rate, a little higher, a little lower, and at 20°C.

(Figure 4-64)

I showed this vugraph 2 years ago, and I have shown it in subsequent papers. Your dotted lines show the theoretical pressure increase. That is, if you just have hydrogen resolution, that’s the rate of pressurizer you would see. Actually, we demonstrated, and these are the average results of about 4 cells of each kind. We can overdischarge 12-ampere hour cells at as high a rate as 100 milliamperes, about C/100, and get pressure equilibrium. The pressure remains constant as we continue to overdischarge. We are plotting pressure versus overdischarge in ampere-hours.

With brand new 24-ampere hour cells, we were able to overdischarge at 400 milliamperes and still attain a pressure equilibrium at a slightly higher pressure. And this represents a C/60 overdischarge rate.

I don’t think the fact that 12-ampere hour cells are now new is as significant as the fact that the design of this 12-ampere hour cell is vintage 1970, and this one 1974. There were some slight changes.
Again this is review. It is a mechanism hypothesized to explain this constancy in pressure as cells are overdischarging.

When a positive cell has exhausted its capacity, hydrogen gas is generated at the positive electrode shown by equation 1. The negative electrode still has capacity, so cadmium continues to discharge to form cadmium hydroxide. The gas that is generated is directly proportionate to the overdischarge current by Faraday's laws.

Some of the gas migrates over to the negative electrode where it is absorbed on the active nickel sites of the negative electrode. So you have got hydrogen being absorbed on sintered nickel forming atomic hydrogen. The hydrogen is removed from the nickel sites by reaction with hydroxide at potential of the cadmium hydroxide electrode. So you remove hydrogen from the nickel and form water.

When you remove hydrogen by the reaction of hydroxide with atomic hydrogen, you have a charge. The cadmium is in intimate contact with the sintered nickel sites containing hydrogen. So the electron that is lost by reaction with hydroxide now reacts with cadmium hydroxide to charge the cadmium hydroxide to cadmium plus two hydroxides. The net reaction is a chemical charging of the cadmium hydroxide by the hydrogen to give you cadmium under water.

The recombination of hydrogen not only removes the gas, but also results in a chemical charging of the negative electrode. Therefore, when you have equilibrium, not only do you retain constant pressure, but you can never fully discharge the cadmium electrode, because as it is discharging electrochemically, it is charging chemically.

An application of hydrogen recombination. Reconditioning by shorting at a battery level to almost zero volts improves the battery characteristics. As Dr. Scott has shown, it extends battery life and also increases the minimum end-of-discharge voltage.

When shorting to zero volts, some of the cells of lower capacity are driven into reversal by the cells with higher capacity. By appropriate selection of a resistor size, pressure buildup is controlled in a reverse state of the art, nickel-cadmium cells.

Improved cells with greater hydrogen recombination capability would permit greater flexibility in choice of reconditioning resistor and reconditioning time. A significant increase in hydrogen recombination capability of nickel-cadmium cells would simplify the battery bypass circuitry, reduce costs, and weight, as well as increase life.
About 1 1/2 years ago, NASA/Lewis gave us a contract to study further hydrogen recombination, get some further evidence about the validity of the mechanism, optimize the parameters that affect hydrogen recombination without detrimentally affecting the capacity or life of a cell in normal use and develop nickel-cadmium cells capable of nondestructive high rate reversals. We are talking about really high rate reversals, gold C/2.

(Figure 4-68)

To further verify the hydrogen-recombination mechanism, we did some AC impedance-mechanism measurements in C2 during over discharge and while we had established equilibrium.

The objective of this was to show that there was no appearing or disappearing short that occurs in the cell that accounts for the constant pressure.

We did the following: We took five 10-ampere hour cells, overdischarged at 50 milliamperes for 40 hours, and we developed pressure equilibrium within the first 10 hours of overdischarge. And the pressure equilibrium was between 34 and 40 psia for the five cells.

The AC impedance measurements remained constant during the overdischarge. There was no short either before or after overdischarge as indicated by charge retention tests.

Finally, the strongest piece of evidence that we are not looking at a short, but we are looking at two hydrogen electrodes, one generating hydrogen, one recombining hydrogen, is that the cell voltage during overdischarge was between 10 and 20 millivolts, and the AC impedance was measured at 2.7 milliohms.

If the voltage were merely ohmic, the voltage that we show here, -10 to -20 millivolts, its value would be $2.7 \times 10^{-3} \times 5 \times 10^{-2}$ or essentially 1/10 millivolt. The voltage that we see is actually two orders of magnitude greater and that seems to support two electrode reaction rather than a short.

(Figure 4-69)

Another thing we wanted to show is that hydrogen recombination that we see on open circuit is consistent specific to hydrogen and not merely the absorption of a gas on a high-surface area electrode.

We ran a couple of cells, and we switched them back and forth, but this is a typical result. A cell when filled with helium on open circuit stand — this is a discharge nickel-cadmium laboratory cell — showed practically no pressure decrease. A similar cell filled with hydrogen shows substantial decrease in pressure.

We switched the cells around, also, putting the hydrogen in one cell, helium in the other cell, and the same result occurred. That is to say, no change with the helium. Pressure decreased with hydrogen.
In order to improve hydrogen recombination, we looked at some of the parameters that, I and NASA Lewis believed, were controlling factors in the rate of hydrogen recombinations.

We looked at two modes of impregnating and negative electrode by electrochemical means and by vacuum. We looked at two levels of precharge on the negative electrode, 40 percent and 20 percent for the positive capacity.

We looked at the effect of electrolyte concentration, 32 percent and 28 percent. We looked at electrolyte fill; that is to say, the percentage of the residual pore volume that contains electrolyte. The residual pore volume of the core, positive, negative, and the separator. We looked at 80-percent fill and 100-percent fill. And finally we looked at the effect of interelectrode distance, 4 mils, 6 mils, and 8 mils.

We were able to control these parameters by measuring the porosity of the electrodes that we used, significant samples of the electrodes. We measured the residual porosity by water absorption, weighing dry and weighing wet, and we calculated the porosity of the separator.

We controlled the interelectrode distance by having a fixed interdistance on the laboratory cell, measuring each electrode, and then by subtraction calculation what the interelectrode distance with the total distance, what the amount of shim would have to be to maintain interelectrode distance of 4, 6, or 8 mils.

The parametric experiment was run in the following way. We had 18 different designs of nickel-cadmium cells, evaluated them for their capability of recombing hydrogen. We had two cells of each kind.

We overdischarged the cells at ever-increasing overdischarge rates, starting at C/100, and then the cells that were able to recombine hydrogen without going into overpressure or undervoltage, they continued on to the next highest rate. But between the time of overdischarges, we readjusted the precharge to its original value by charging the cells and venting oxygen.

The experiments for cells made with electrochemically impregnated negatives have been completed. What we have achieved there is an optimum hydrogen recombination rate of C/20 which is three times as high as anything achieved in the state of the art with cadmium cells.

The design parameters were 6-mil interelectrode distance, 40-percent recharge, 32-percent electrolyte and 100-percent electrolyte fill.

I am aware that yesterday a statement was made regarding the optimum rate that we achieve is C/2. We did, indeed, do this. The work is going on right now with vacuum impregnated negative
electrodes. We have achieved this in quite a few cells. But I am not ready to go into the details of this. That will be the subject of some future paper.

(Figure 4-72)

For the two cells of optimum design, we plotted equilibrium pressure versus overdischarge rate, and each data point represents the pressure where the cells remained constant during a particular overdischarge rate.

We see that cell equilibrium pressure is directly proportional to overdischarge rate and essentially the two curves pass pretty close to the origin, zero, which is in agreement with the hydrogen recombination hypothesis.

(Figure 4-73)

Here's a summary of the different values attained under different conditions, different values of hydrogen recombination rate expressed at the current density under different test conditions; open circuit, best state-of-the-art, nickel-cadmium cell gives you a recombination current density of 0.43 milliamperes per square decimeter. That's the geometric surface area of the negative electrode of that cell.

The best laboratory cell, or laboratory cell unoptimized, gives us about the same thing, 0.33 milliamperes per decimeter squared.

During discharge where the potential of the negative is more favorable to hydrogen recombination, we have an order of magnitude increase in the hydrogen recombination rate from 0.3 to 3.0 going from open circuit to discharge.

When we go to overdischarge, the best state-of-the-art nickel-cadmium cell is 36, unoptimized laboratory cell is 9, the optimized laboratory cell is 93. So we have a threefold increase.

If we consider the data we obtained with the vacuum impregnated cells, we have 900 milliamperes per decimeter squared that we have attained, but that will not be discussed today.

(Figure 4-74)

Our future work on this contract is completion of the parametric experiment for vacuum impregnated cells, vacuum impregnated negatives. As to the optimization with relation to active material loading, we are going to look at loading levels on the negative electrode of 2.1, 1.8, and 1.4 grams per cc void, and evaluate as we did before, ever-increasing overdischarge-rates.

We will then fabricate 24 identical optimized laboratory cells and subject them to geosynchronous orbit cycling with periodic reversals and sequential removal of cells for teardown analysis at the end of each season.
The teardown analysis will consist of determining electrolyte distribution, electrolyte concentration, plate capability — that is flooded capacity of the plate — undischargeable cadmium, physical dimensional changes of the electrodes, separator condition and thickness. And finally that should be one dot out here.

As a follow on to this work, we would procure and have fabricated flight type cells of the optimum design, and we would then test as a battery.

DISCUSSION

KILLIAN: Paul, you showed very different recombinations depending on whether it was open circuit discharge or overdischarge slide. Do you have an explanation for that?

RITTERMAN: Yes. On discharge you have a polarization of a negative electrode, which favors hydrogen recombinations, and have bigger delta V between the hydrogen cell and the cadmium hydroxide cell. Open circuit you have a very small potential difference. You have got 20 millivolts.

With respect to overdischarge — and this is something I have observed — the electrolyte seems to disappear on overdischarge, decreasing the thickness of the diffusion layer and making the hydrogen more accessible to the cadmium electrode.

SCHULMAN: How important is this state of precharge on this recombination mechanism?

RITTERMAN: You mean the amount of charged cadmium that’s left?

SCHULMAN: Yes. I thought I heard you mention that you had to sort of rejuvenate the precharge.

RITTERMAN: You have got to understand what I am doing here. I am overdischarging my cell at various rates. For example, I overdischarge at C/100 and I develop 50 pounds of hydrogen pressure. Okay?

I don’t want to wait and sit around until that hydrogen recombines, so what I do is pump the hydrogen out and I say that hydrogen is equivalent to a certain amount of ampere-hours of negative precharge, and I hold the cell. I have got to return to the cell.

So, in order for me to go on to the next reversal rate at the same state of charge of the negative electrode that I was in initially, I have got to charge up that cell, overcharge it, and then to oxygen and then get back to the original state. Then I short the cell down and I have got the cell in a state that I was in before I had the previous overdischarge.

O’SULLIVAN: Could you tell us where the electrochemical plates were from? If there was any nickel hydroxide in the negatives?
RITTERMAN: They were made by GE. This is for the parametric tests we are talking about. There is another manufacturer, Gulton. But for the parametric tests made by electrochemical impregnation at GE. And to my knowledge, no intentional nickel hydroxide is in there.

O'SULLIVAN: Where they analyzed for it?

RITTERMAN: No, they were not.

HARKNESS: Paul, one question on the 24 cells you are going to make, will they be electrochemically impregnated?

RITTERMAN: Probably not, based on results that we are not ready to report on. But based on the C/2 rate, they would not be electrochemically impregnated, but they would be vacuum impregnated.

NEWELL: Were you concerned about the electrolyte concentration when you were venting hydrogen and oxygen?

RITTERMAN: I gave that some thought. The change was very slight. Water weighs 18, and 18 is 26 ampere-hours, so you have a relatively small change based on the amount of electrolyte we had in there. But, no, I did not provide for that small change.

GROSS: When you forced the cell into overdischarge, this sets up a driving force which tends to plate out cadmium and increase the likelihood of shorting. This becomes a greater problem, especially when the cell gets old and has been observed on discharge of old cells.

It would seem therefore, that in the optimization of the whole design, in looking at the whole problem, this aspect of the problem would certainly have to be taken into account.

RITTERMAN: I don’t know if I can just answer with a simple yes or not, but I think cadmium was more likely to do this on overcharge than overdischarge.

GROSS: It occurs on overdischarging.

RITTERMAN: Are you saying that the cadmium is plating out of the positive electrode toward the negative electrode?

What you are doing is that you are driving the positive electrode to the potential of cadmium hydroxide. Is there a cadmium hydroxide in the electrolyte, is what you are saying that tends to plate out?

GROSS: If, for example, you had cadmium hydroxide on the nickel positive....

RITTERMAN: Deliberately put in there?
GROSS: Let’s say it’s there by migration. Then it will be reduced cadmium. If it is then in contact with cadmium hydroxide in the separator, it will reduce that and that could accelerate. You are shorting through the separator giving you a cadmium dendrite.

RITTERMAN: Right. But the negative electrode is all cadmium, and when you charge that, it is a much more favorable reaction to occur — growth from the cadmium out toward the positive and there is very rarely a short on overcharge.

GROSS: That’s another problem, but that’s not the problem we are addressing. The problem we are addressing is the tendency for cadmium to short out the cells on overdischarge. There is no question that there is a driving force; there is no question that it sometimes happens especially in old cells. The problem is to properly take that risk into account.

RITTERMAN: I think we are going around in circles now. I will discuss it with you privately if you wish.

GOUDOT: Did you check the curve of evolution of gas as a function of DOD?

RITTERMAN: I am sorry — you are saying the evolution of gas as a function of DOD?

GOUDOT: Yes.

RITTERMAN: Well, there is no evolution of gas under the normal DOD.

GOUDOT: No. When you made the cycle with different DOD and going in a reverse way, did you observe a plateau, for instance?

RITTERMAN: These parametric testings were new cells. We did nothing to them except give them 30 conditioning cycles and then start the reversal right away.

GOUDOT: But did you observe a plateau before, a relaxed time before evolution of gas due to that?

RITTERMAN: Are you saying a residual time to antipolar mass, or what?

GOUDOT: Nonfunction of DOD in the cycling.

RITTERMAN: There is no DOD.

GOUDOT: It is 100 percent each time?

RITTERMAN: 100-percent discharge, yes. And then overdischarge. We start out okay, and we set precharge on the cell, initially at 40 percent, for example. We then discharge the cell completely, we short it down, we proceed to overdischarge, and we get a certain amount of hydrogen there at an equilibrium pressure.
Rather than wait for hydrogen to recombine and return the cadmium to its original state of charge, we vent the cadmium, charge the cell all the way up again, and vent the oxygen — this time to reset the precharge to its original value, and we know this because we know the value of the pressure of hydrogen. So half that pressure of oxygen is needed to reset the precharge. We short the cell down again, and then we start the overdischarge.

So, each time we start out with a completely discharged cell with respect to the positive electrode and at the same precharge with respect to the negative electrode.

LACKNER: I just wanted to get a clarification on your terminology, “100-percent electrolyte fill.” Is there some way you could translate that into cc’s per ampere-hour?

RITTERMAN: No. You could, but it wouldn’t mean anything because the residual porosity of electrodes vary. What we did is, measure the porosity of a good sample of the electrodes that we used, residual porosity.

LACKNER: You are filling all available pores, then?

RITTERMAN: We are filling all available pores, yes. We can calculate the porosity of the separator. It is under specific compression of the interelectrode distance that we set.

LACKNER: That’s the porosity of the plate originally not taking into account any changes that might have taken place?

RITTERMAN: I take the original porosity. I don’t preswell the plates or anything like that.
**NI-CD CELL REVERSAL BACKGROUND**

- **Positive Limiting** Ni-Cd cells evolve hydrogen when driven into reversal.
- **One Ampere Hour of Reversal** results in sufficient hydrogen evolution to increase pressure 120 psi.
- On an ampere hour basis, theoretical hydrogen pressure build-up during reversal is extensive. However, it can be kept at a minimum and even at zero by selection of low reversal rate.
- **Constant Current Reversal** using aerospace Ni-Cd cells have shown that a steady state condition is achievable at C/100 and temperatures of 20°C.

**Figure 4-63**

**HYDROGEN RECOMBINATION MECHANISM**

- When the positive electrode has exhausted its capacity, hydrogen gas is generated within the cell at the positive electrode:
  1. \(2 \text{H}_2 \text{O} \rightarrow 2 \text{H}^+ + \text{O}_2\) and while the negative electrode is discharging,
  2. \(\text{Cd} + 2\text{OH}^- \rightarrow \text{Cd(OH)}_2\)
- The \(\text{H}_2\) generated is directly proportional to the overdischarge current.
- Some of the hydrogen gas migrates over to the negative electrode where it is absorbed on the sintered nickel sites:
  3. \(\text{H}_2 + \text{Ni} \rightarrow 2\text{NiH}_2\)
- Hydrogen is removed from the nickel sites by reaction with hydroxide at the potential of the \(\text{Cd}/\text{Cd(OH)}_2\) electrode:
  4. \(2 \text{NiH}_2 + 2\text{OH}^- \rightarrow 2 \text{H}_2\text{O} + 2 \text{Ni}^+ + 2\text{e}^-\)
  5. \(\text{Cd(OH)}_2 + 2\text{e}^- \rightarrow \text{Cd} + 2\text{OH}^-\)
- For a net reaction of (3) + (4) + (5):
  6. \(\text{Cd(OH)}_2 + \text{H}_2 \rightarrow \text{Cd} + \text{H}_2\text{O}\)
- The recombination of hydrogen not only removes the gas but also results in "charging" of the negative electrode.
- When the rate of hydrogen generation equals its rate of recombination, equilibrium is reached and the cell can be overdischarged indefinitely without change of pressure or state of charge.

**Figure 4-64**

**APPLICATION OF HYDROGEN RECOMBINATION**

- **Reconditioning** by shorting at a battery level to almost 0.0V battery voltage has resulted in:
  - Extension of battery useful life
  - Increase in minimum end of discharge voltage.
- When shorting to almost 0.0V, on a battery level cells of lower capacity are driven into voltage reversal:
  - By appropriate selection of reconditioning resistor size, pressure build-up is controlled in reverse state of the art cells.
  - Improved cells with increased hydrogen recombination capability would permit greater flexibility in choice of reconditioning resistor and reconditioning time.
- A significant increase in hydrogen recombination capability of Ni-Cd cells would simplify battery by pass circuitry, reduce cost and weight as well as increase life.
OBJECTIVES

- Verification of the hydrogen recombination mechanism.
- Optimization of design parameters that affect rate of hydrogen recombination without detrimentally affecting normal cell performance.
- Development of Ni-Co cells capable of non-destructive high rate reversal.

Figure 4-67
Pressur e decay cell of Ni-Co laboratory on open circuit filled with helium and filled with hydrogen.

Figure 4-68
Design parametric experiment.

### Table
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<tr>
<th>Method of Negative Electrode Impregnation</th>
<th>Pressure (psi)</th>
<th>Electrolyte Concentration (M)</th>
<th>Inter-electrode Distance (mil)</th>
<th>Inter-electrode Distance (mil)</th>
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Figure 4-69
OPTIMIZATION OF HYDROGEN RECOMBINATION CAPABILITY

- PARAMETRIC EXPERIMENT
  - 18 DIFFERENT DESIGNS OF NICKEL CADMIUM CELLS EVALUATED FOR THEIR CAPABILITY TO RECOMBINE HYDROGEN.
  - CELLS OVERDISCHARGED AT EVER INCREASING RATES
    - C/100  C/50  C/20  C/5  C/2
  - OVERDISCHARGE TERMINATED WHEN CELLS REACH OVERPRESSURE (60/120 PSIA) OR UNDERVOLTAGE (-0.5V).
  - EXPERIMENTS FOR CELLS MADE WITH ELECTROCHEMICALLY IMPREGNATED NEGATIVES HAVE BEEN COMPLETED.
  - DESIGN WITH OPTIMUM HYDROGEN RECOMBINATION (C/20 ACHIEVED)
    - 6 MIL INTERELECTRODE DISTANCE
    - 40% PRECHARGE
    - 32% ELECTROLYTE
    - 100% ELECTROLYTE FILL

Figure 4-71

RATES OF HYDROGEN RECOMBINATION EXPRESSED AS CURRENT DENSITY (PER UNIT NEGATIVE ELECTRODE SURFACE AREA)

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<tr>
<th>CONDITION</th>
<th>CELL</th>
<th>CURRENT DENSITY*</th>
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<tbody>
<tr>
<td>OPEN CIRCUIT</td>
<td>BEST STATE OF THE ART Ni-Cd</td>
<td>0.45 mA/cm²</td>
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<td>LABORATORY Ni-Cd (UNOPTIMIZED)</td>
<td>0.35 mA/cm²</td>
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<td>DISCHARGE</td>
<td>LABORATORY CELL (UNOPTIMIZED)</td>
<td>3.0 mA/cm²</td>
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<td>OVERDISCHARGED</td>
<td>BEST STATE OF THE ART Ni-Cd</td>
<td>36.4 mA/cm²</td>
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<td>UNOPTIMIZED LABORATORY CELL</td>
<td>9.4 mA/cm²</td>
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<td></td>
<td>OPTIMIZED LABORATORY CELL</td>
<td>93.8 mA/cm²</td>
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*AT Pressures of 50-80 PSIA

Figure 4-72

EQUILIBRIUM PRESSURE VS. OVERDISCHARGE RATE FOR TWO CELLS OF OPTIMUM DESIGN

FUTURE WORK

- COMPLETION OF PARAMETRIC DESIGN EXPERIMENT
- OPTIMIZATION WITH RELATION TO ACTIVE MATERIAL LOADING OF NEGATIVE ELECTRODE
  - LOADING LEVELS
    - 2.1 g/cm³  1.8 g/cm³  1.4 g/cm³
- FABRICATION AND CYCLING OF 24 IDENTICAL OPTIMIZED LABORATORY CELLS
  - SIX SEASON OF GEOSYNCHRONOUS ORBIT WITH PERIODIC REVERSAL
  - SEQUENTIAL REMOVAL OF CELLS FOR TEAR DOWN ANALYSIS
- TEAR DOWN ANALYSIS OF CELLS
  - ELECTROLYTE DISTRIBUTION
  - ELECTROLYTE CONCENTRATION
  - PLATE CAPABILITY
  - UNDISCHARGEABLE CADMIUM
  - PHYSICAL DIMENSION OF ELECTRODES
  - SEPARATOR CONDITION AND THICKNESS
  - FABRICATION AND TEST OF FLIGHT TYPE CELLS OF OPTIMUM DESIGN

Figure 4-74