

REVERSAL OF NICKEL CADMIUM CELLS

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We have been doing a limited number of experiments right along. We don't vent the hydrogen off in general over the last year or year and a half with two cells. I need to emphasize that these are a different design nickel-cadmium cell, the same manufacturer that Paul has been talking about. We have seen some different behavior that I would like to report.

(Figure 4-75)

The areas I am going to talk about, first, is a mistake that gave us some information. Second, most of the time is misspent looking at the kinetics of the reaction of hydrogen on open circuit stands after high-rate reversal of the cell. We are talking about high rate here as $C/5$. And, finally, we have looked briefly at the pressure voltage profiles during low-rate reversal, similar to what Paul has been saying.

I need to emphasize the order we have done the experiments in, which may have a bearing on it, is as shown here.

(Figure 4-76)

The two cells we have been working with are as described here. They have a common case in negative. We merely turned the little copper connector solder lug off the top of the cell, drilled 1/16 inch hole into the interior itself, and hooked up a pressure transducer with the valve.

(Figure 4-77)

We have seen no effects of that type of procedure in the behavior of the cell.

First hydrogen – the study of hydrogen addition to a cell. We set the thing up and were cycling it, but it developed a leak in the plumbing, causing us to lose the precharge. So, by having a cell with no precharge in it, we had a problem and we simply added hydrogen to it to regenerate the precharge.

I have shown how much precharge we measured by electrochemical means just in the cell. This is a starved cell. It was not opened, indicating the reactions as Paul indicated. It goes as shown with that type of stoichiometry.

What I would like to point out, you will see later, is the rates we observed for hydrogen recombination. Those are in reciprocal hours. These are not rapid experiments.

(Figure 4-78)

The second area has to do with the effects of high-rate reversal on the cells and subsequent pressure, hydrogen pressure loss. The regime that we have adopted for these experiments is shown. Most of the time we charged the cell up and measured the capacity. That's simply what the first two steps are for.

Notice that for a particular experiment, we would charge it for 1 hour at the two-ampere rate, C/5 rate, and then drive it into reversal or whatever the pressure is that we wish to start it at was. Then switch the cell open circuit and continuously monitor all those good things.

We corrected all the pressures to 24 degrees so they could be compared. The temperatures we used were shown. 22 degrees was not in the thermostat, so the swing was plus or minus 2 degrees.

(Figure 4-79)

During the reversal, we see a variety of types of behavior. We see initially no pressure increase in the voltages shown below. This, we assume, is from one of two things: either cadmium-hydroxide in positive electrode or residual nickel oxide positive capacity that is being discharged out.

Then we have a slowly changing voltage. Then we see a very, very high linear pressure increase. The slope of that line is about 80 percent of the theoretical we predicted and was all being converted into hydrogen. One thing you can note from that line is where the other 20 percent is. We are not sure, but it certainly isn't by first order of combination of hydrogen, or it would curve over. But it is straight.

I will show the recombination hydrogen reaction curves here that bear some correlation to that. However, we do not always see that step, the plateau in pressure at the first of the reversal, as is shown here where it turns up quite rapidly. The slope of this line and this line are different, and these are different reversals. These are the same.

In fact, no matter what the current is and we have a pressure rise like this, we see the same slope in that line, whether it be 2 amperes or 100 milliamperes.

(Figure 4-80)

The loss of pressure now – we have two sections that I have shown – we have good first-order kinetics after about 24 hours, and the line shown there is more linear regression on that first-order kinetics section. Before that we always see a higher rate.

It is totally uncorrelatable in order with hydrogen.

The interesting thing is that the initial slope of this line is very similar to the slopes of these lines.

It may well be that we have clearly another process going on. The time would indicate to me that it is not pressure that is causing this increase rate — I mean it's not oxygen. I don't know where we would get the oxygen in this case. It's not temperature because of the duration, and the fact that these experiments are done in a thermostat with good thermal control.

(Figure 4-81)

Summarizing the data over the temperatures, we get a little bit better than a factor of two. Repeatability between experiments. Notice the pressures that we have been running into, some in excess of 300 pounds.

Our objective in these experiments initially was that if you ever got in that situation, what do you do about it. Our conclusion so far is not much.

Notice the experiment numbers here are the order of experiments shown, so that nine is the last experiment in the capacity frequently. I have also added in here our rate constants for hydrogen additions. This is done only on one cell. We got only one leak.

Notice the comparison between the 22 degrees and 22 or 24 degrees here and the rate constants. One of these experiments, I believe it was seven, was done with the cell short circuited rather than open circuit for part of the time. We saw no difference in the rate.

(Figure 4-82)

Again, this is just an Arrhenius plot showing the temperature dependence, and I think this agrees quite well with Paul's statement which he's previously seen for open circuit reactions.

Having done that and getting these cells at very high pressures, we begin to ask, what can we do about it?

(Figure 4-83)

The first thing we tried was to reverse the cell at high rate to a given pressure and then to switch to a low-reversal curve and to watch what would happen.

What happens is that we see an initial rapid pressure decrease here, correlating with what I showed you before on the first-order plot. This rapid decrease in pressure initially occurred after a reversal, then a rise with a slope in this line, psi per ampere-hour is equal to the slope at 2-ampere rate, and then a falloff in pressure, first order of decay.

This is the voltage down here. You can see that the voltage behavior comes up and becomes constant at very near zero on the order of 10 to 30 millivolts. If we increase the reversal current to 200 milliamperes, it increases in what is essentially an ohmic fashion. In both cases, you notice that the two cells are not alike, but we have similar behaviors.

At the point when the pressure had decreased to essentially a few psi, we then measured the ohmic behavior in this, called "Ohm's Law" both in the reversal direction, in the charge direction as long as the current wasn't too low to leave it in the charge direction very long, that short immediately opens, and everything looks fine.

We subsequently started from a fully charged cell and discharged it constant current at 100 milliamps, which is $C/100$. We again see the pressure buildup and this type of voltage behavior, and then the cell apparently shorted. Now, what I am talking about a short here is that we get "Ohm's Law" behavior for current flow in both directions through zero.

Under other conditions, we have tried to do this on a cell we know is open circuited. We don't get that kind of behavior at all. So we would interpret that as being short.

(Figure 4-84)

Summarizing, in all of our experiments, actually the first thing is, in high rate reversal, we have never seen any shorting. These cells are open circuit, and they behave like an open circuit cell.

If we reverse to say 150 psi, the voltage will slowly wiggle around like this to a positive 1.2 volts on open circuit. If you really reverse it hard, it will stay very near zero for as long as you allow these to run and until the pressure is down. But we've never seen shorting.

However, when we go to low rates, $C/50$, $C/100$, we have reproducibly seen shorting. Furthermore, the rates of hydrogen loss in these cells after you have established the pressure someplace are essentially the same whether the cell is under low rate reversal conditions, open circuit, or internally or externally shorted.

Finally, what we think is an ohmic short can be destroyed simply by allowing the cell to stay in open circuit or putting it on charge. And we have seen no ill effects. We still have the capacity we started with in these cells after about a year and approximately ten reversals. So we had good voltage behavior, and we have seen no real ill effect of this repeated high pressure reversal in the cells.

DISCUSSION

BADCOCK: I would like to ask Paul a question, and he's going to ask me one on his cells. Did you have any problems with overcharged pressures on your cells with large amount of electrolyte in them?

RITTERMAN: No. It's not really a large amount of electrolyte when you consider 100-percent fill. It's not based on any ampere-hours.

Now, may I ask you a question? You showed a curve where you had a very high recombination rate initially an open circuit. If you would show that again — you showed a pressure

decay of hydrogen versus time on open circuit. That's very high. That initial part, is that what you obtained immediately after you reversed the cell?

BADCOCK: Yes, that's immediately after we had reversed the cell on open circuit.

RITTERMAN: So, wouldn't that be a residual effect of the higher rate, the high reserve, anyway?

BADCOCK: That is a very good point. I think it would be — I wondered why we haven't seen the same type of effects that you have in many instances. And I think that this and the less than theoretical slope on the lines during reversal have bearing on — that we have another mechanism going on in these cells.

Now, why haven't we seen it in these cells? I should have mentioned the age of these cells. They were about 5 years old. We had only about 200 cycles on them when we started. They also have puffy tops on them. Now, that's been corrected in the volume because of the high pressures. But again no problem.

RITTERMAN: What was the separator?

BADCOCK: These are polypropylene separated cells.

RITTERMAN: I don't know if it would make a difference, but all my tests were done with pellon separators.

BADCOCK: I understand.

ARMANTROUT: Chuck, I assume you had the same negative electrode in your cells as Paul did?

BADCOCK: No. I would like to tell you whether it had a silver additive or not, but I am not sure.

ARMANTROUT: Would you speculate as to what might have happened had your electrodes been teflonated?

BADCOCK: No.

ARMANTROUT: I did not find hydrogen recombination with teflonated negatives.

BADCOCK: Did you wait long enough?

ARMANTROUT: Yes. I found ultimately some recombinations, but I didn't find a plateau. The slope was going right up.

BADCOCK: Remember, we have not seen a plateau at any high rate. At low rates, the only time we see a plateau is when we would interpret the cell starting to short.

We were looking for that intermediate behavior Paul has reported on. We haven't seen that in this case.

RITTERMAN: What you have always done though is that you have gone from a high rate overcharge, switched down to either open circuit or a low rate overdischarge. Is that correct? High rate over discharge and then shut down to low rate?

BADCOCK: We have seen exactly the same behavior as when we started with a fully charged cell at constant current discharge, C/100, and took it all the way down and into reversal. That was our simulation of reconditioning.

RITTERMAN: The new cell that you ran these tests on, were they the exact same history as far as you know?

BADCOCK: Yes. Came out of the same cell pattern.

SEIGER: Could you tell me what the precharge is on these cells, and also what the interelectrode spacing was?

BADCOCK: I can't answer the interelectrode spacing. It was essentially 8- or 10-mil, polypropylene in these cells. The precharge is set at about 5 ampere-hours in these cells. That's about 25 percent of the total negative electrode capacity.

We have measured, in some cases, that there's greater than 2.9 ampere-hours, because that's how much we needed to get to that pressure.

SEIGER: Would you suspect that any of the positive electrodes would have swelled to alter the interelectrode spacing?

BADCOCK: Yes, I do expect a little bit. I can't answer these questions until we are through with these cells and cut them apart. But they are test specimens right now, so we don't want to violate them.

LIM: Can you extract activation and energy from your Arrhenius plot?

BADCOCK: Yes. It was 14 plus or minus about 2k cal's per mole.

SCOTT: Can you say in general or in particular, how many ampere-hours total reversal that you had at these various rates when you saw the shorting pattern?

BADCOCK: On the one where we reversed a cell from full charge, took it into reversal at 100 mils, we had less than 2-ampere hours reversal in the cell, considerably less than that.

In general, it has been between 2 and 3, 3 1/2 ampere-hours when we have seen them, what I interpret as short.

RITTERMAN: Chuck, you showed some pressure buildup at C/5 discharge rates. You said you got about 80 percent of the pressurizer you expected to get. You also stated there was no short during that time.

BADCOCK: Yes.

RITTERMAN: Would you attribute the other 20 percent to hydrogen recombination?

BADCOCK: I can't say that. I should emphasize that not only did we see that same slope in psi per ampere-hour at 2 amperes, but also we see it at 100 milliamperes. If it is hydrogen recombination occurring during that time, it is not dependent on the pressure of hydrogen, which is certainly a reasonable thing to assume in some cases. If your coverage is near 100 percent

RITTERMAN: The one you have got to be aware of is that you do have an unaccounted for coulombic anomaly. If it isn't hydrogen recombination and there isn't a short, where did that 20 percent go?

BADCOCK: I would like to know.

GROSS: I presume that the activation energy that you calculated agrees with the cadmium hydroxide reduction. Is that correct?

BADCOCK: I don't know that. I have been looking for what that activation energy is. I know it's not diffusion or hydrogen. It is too slow wrong activation energy. I think it is the H₂ or H adsorb electrochemical reaction that has that thermal activation energy. There is some literature which would indicate that. I think that's what it is, but I'm not sure.

GROSS: I wonder also, if perhaps you had calculated and extrapolated an Arrhenius curve to get the activation energy at the very beginning of the recombination where you had a much higher slope, possibly try to pick out what reaction that might have been.

BADCOCK: To do that, you must have a constant order in the kinetics. The problem is when I tried to do a log/log plot to determine the order of the kinetics there, I get numbers between a 4 and 10 for order and hydrogen. So there is a problem there, and it is not constant.

I should point out that area is not constant enough in rate so one can do anything with it. It is not that predictable. It occurs every time, but not in a reproducible or predictable fashion.

SEIGER: Paul Ritterman had said something about the disappearing of the electrolyte when he went into reversal. I have observed it, and others have observed it. Perhaps during that initial period of time, the area involved in the recombination is different than it is a little later on.

BADCOCK: We have some data that we have to process yet and some other data to bear on that. The interpretation becomes a lot more complex than one would wish, and that's why I am not discussing that.

SEIGER: It might not be chemical. It might be something physical.

BADCOCK: Yes.

RITTERMAN: Again, going back to that log plot that you showed, I am not quite sure whether you said that initial high rate of recombination occurs only immediately after extensive overdischarge, or it would occur when you had a cell sitting in a completely discharged state for a while, dormant, and you added hydrogen?

BADCOCK: When we have added hydrogen to the cell, it does not occur. It is related to the high rate – at least our data indicate that it is related to the high rate of reversal.

RITTERMAN: You mean it is related to some intermediate situation?

BADCOCK: Obviously, one explanation for this is that during a reversal you generate reactive sites that recombine hydrogen very efficiently. But they are lost very rapidly. What you are seeing there is a loss in a number of active sites. That is a nice thing. We haven't anything to demonstrate that, but that is a nice explanation because it agrees with a less-than-theoretical slope during the reversal itself.

RITTERMAN: Only under the conditions where you shut off the cell after extensive reversal did you see that?

BADCOCK: That's correct. I guess one comment I would like to make. I think these data show you the range that one might expect in cells for the behavior during or after reversal. I don't disagree with the TRW position on the effects of reversing a cell. But if you are planning to do that, I think that every cell design, and hopefully the lot that you are using, is tested to make sure that you get their behavior rather than my behavior.

Area of investigation

- ADDITION OF H₂ TO A CELL (open circuit)
- KINETICS OF H₂ REACTION ON OPEN CIRCUIT STAND FOLLOWING HIGH RATE (C/5) REVERSAL
- PRESSURE AND VOLTAGE PROFILES DURING CONTINUOUS LOW RATE REVERSAL

Figure 4-75

H₂ Addition to a Cell

- CELL WAS CYCLED: 2.5 Ah CHARGE @ 2 amp
2 Ah REVERSAL @ 2 amp
12-hour OPEN CIRCUIT STAND
- LEAK CAUSED LOSS OF PRECHARGE TO APPROXIMATELY 1 Ah
- H₂ ADDED TWICE FOR A TOTAL PRESSURE REACTED OF 338 psi (2.78 Ah)
 - RATE CONSTANTS FOR H₂ LOSS: 4.9 AND 4.6 x 10⁻³ hour⁻¹
- SUBSEQUENT REVERSAL SHOWED AN INCREASE OF 1.7 Ah IN PRECHARGE (~60% of 2.78 Ah)

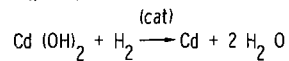


Figure 4-77

Experimental Arrangement

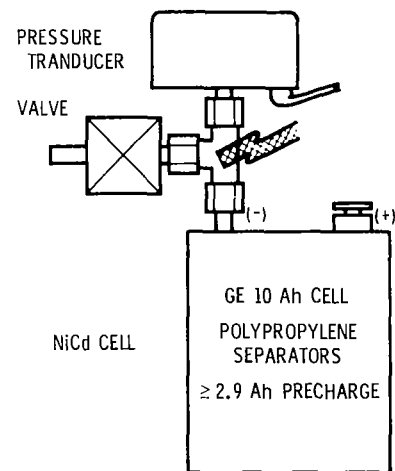


Figure 4-76

Observations During Reversal and Kinetics of Loss of H₂ from Reversed, Open Circuit Ni Cd Cells

- PROCEDURE:
 - CHARGE AT C/10 FOR 16 hr (optional)
 - DISCHARGE AT C/2 (5.0 amp) TO 0 V (optional)
 - CHARGE AT C/5 FOR 1 hr
 - DISCHARGE AT C/5 INTO REVERSAL UNTIL DESIRED PRESSURE OR -0.5 V IS REACHED
 - OPEN CIRCUIT
- CONTINUOUSLY RECORD VOLTAGE AND PRESSURE
 - PRESSURES CORRECTED TO 24°C
- TEMPERATURES USED: 40, 32, 24, 22, 9.5°C

Figure 4-78

Voltage and Pressure During C/5 Reversal

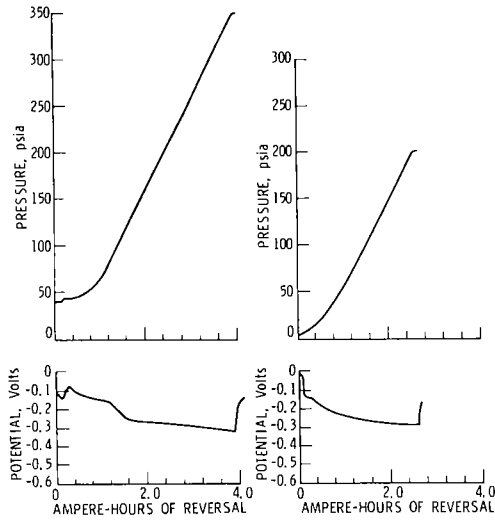


Figure 4-79

Summary of Data for Open Circuit Stand Experiments

EXP No.	TEMP °C	P ₀ psia	CELL A CAPACITY Ah	(k) × 10 ⁻³ hr ⁻¹	P ₀ psia	CELL B CAPACITY Ah	(k) × 10 ⁻³ hr ⁻¹
6	9.5	266	11.2	2.1	250	11.6	1.5
1	2.2	258	11.9	6.2	334	12.6	4.9
5	2.4	111	11.7	5.7	148	12.3	5.0
7	2.4	252	--	11.1	236	--	5.5
8	2.4	250	12.2	5.3	234	12.4	2.6
9	2.4	251	11.8	6.9	236	12.0	5.4
4	3.2	243	--	11.4	228	--	9.6
2	4.0	242	11.1	33.4	225	12.3	21.7
3	4.0	159	--	20.1	138	--	12.9
H ₂ ADD'N	2.2	--	--	4.9			
				4.6			

Figure 4-81

Log P(H₂) vs Time for H₂ Reaction Cell A, Experiment 5, 24°C

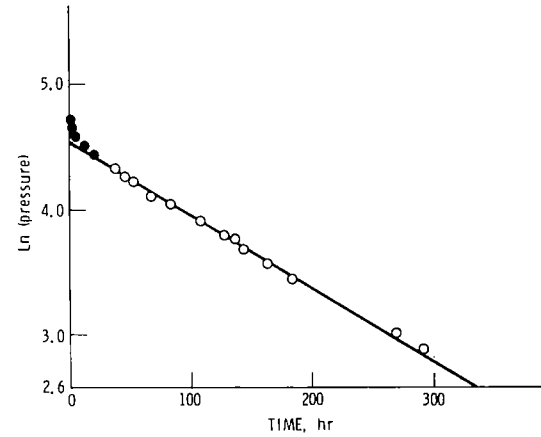


Figure 4-80

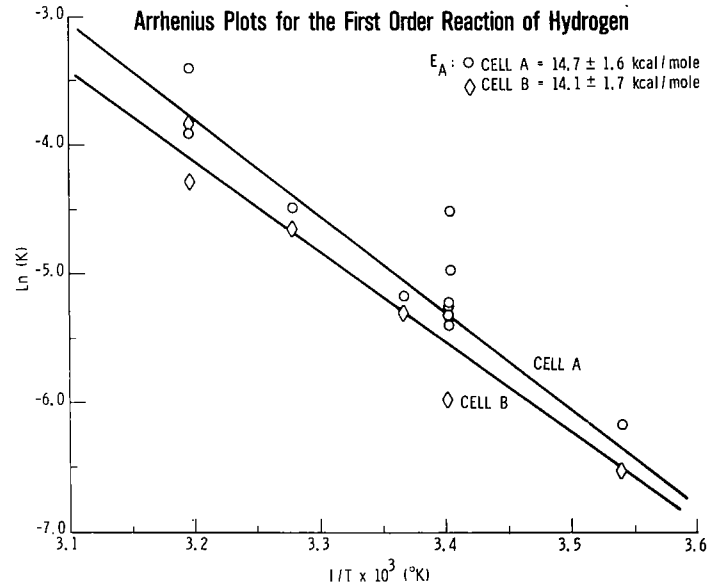


Figure 4-82

Pressure and Voltage Behavior During Constant Low Rate Reversal After High Rate Reversal

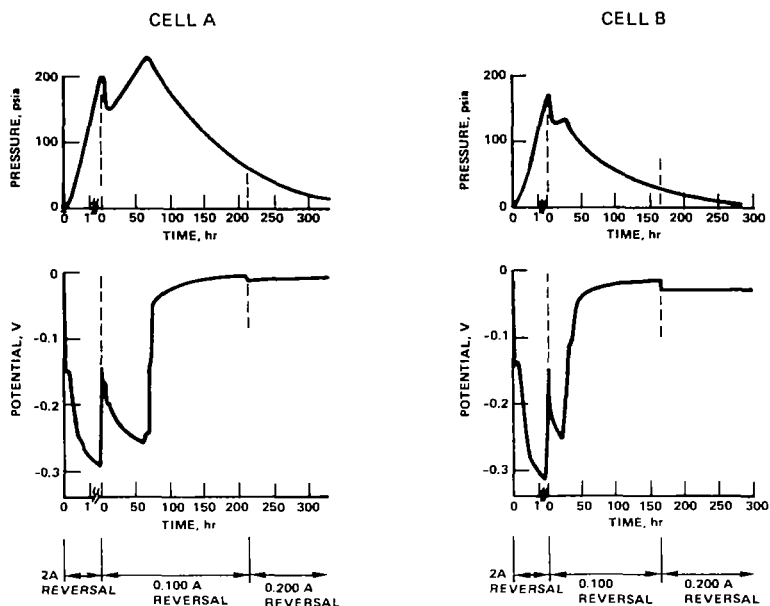


Figure 4-83

Results of Low Rate Reversal Studies

- CONTINUOUS, LOW REVERSAL CURRENTS (C/50, C/100) EVENTUALLY RESULT IN OHMIC SHORTING IN THESE CELLS
 - NO SHORTING WAS OBSERVED DURING HIGH RATE REVERSALS
- RATE CONSTANTS ARE SIMILAR UNDER ALL CONDITIONS AT 24°C FOR H₂ DECREASE

	CELL A (K) x 10 ⁻³ hr ⁻¹	CELL B (K) x 10 ⁻³ hr ⁻¹
LOW RATE REVERSAL (after high rate reversal)	10.0	10.7
LOW RATE DISCHARGE AND REVERSAL (C/100)	6.4	4.7
OPEN CIRCUIT AFTER HIGH RATE REVERSAL	7.3 ± 2.7	4.6 ± 1.4

- THE OHMIC SHORT FORMED DURING LOW RATE REVERSAL IS REMOVED BY OPEN CIRCUIT STAND OR BY CHARGING (C/10)
 - NO ILL EFFECTS OF SHORTING OR REVERSAL HAVE BEEN DETECTED IN THE ELECTRICAL PERFORMANCE

Figure 4-84