

THE PRACTICAL LIMIT OF LOADING NICKEL HYDROXIDE ELECTRODES

E. McHenry
Bell Laboratories

This is a presentation of a previously unreported investigation of the practical limit of loading nickel hydroxide electrodes.

Originally, I had intended to study the effect of compression on the positive electrodes. It is presumed that as you compress the electrode, you would restrict the size of the pores; you would develop an IR path, the electrolyte would not be able to get into the inside pores, and then the efficiency of the electrode would drop off. All the electrodes I used here were 1 inch by 2 1/4 inch by 28 mils thick.

(Figure 5-62)

It shows here originally on the unimpregnated plaque as it was compressed with very little compression, there was considerable distortion, until finally it collapsed all the pore structure and now the compression is trying to collapse the particles themselves.

You see a similar thing in the electrode which is loaded with nickel hydroxide. But we reach this plateau at a smaller amount of thickness. It runs into this problem as you compress a very low amount, because you have more material in there.

(Figure 5-63)

The most striking thing is that you can compress it up to 20,000 kilograms per square centimeter which is very close to the yield point of low carbon. You find that there is no real change in capacity: no loss. As a matter of fact, the capacity is better, so apparently there are not pores in the nickel hydroxide electrodes while it is running.

These were all done while they were wet, full of electrolyte, and they were compressed without drying. So that the actual working nickel hydroxide apparently is much more voluminous than nickel hydroxide is dried. Apparently, it is hydrated, and the hydrogen ions apparently just migrate right through the active material itself. They don't appear to need any electrolyte path to get inside the electrodes.

At that compression there certainly couldn't be any — there could be a few blind pores, but no continuous pores to the outside, or the electrolyte would leak out through them.

(Figure 5-64)

This is just a group of electrodes which were impregnated to different numbers of cycles, different loadings. As you compress the electrode, you will find at very low loadings that if you

measure the volume of the electrode, you subtract out the nickel volume, then you have the volume of nickel hydroxide left over, and calculate a density of nickel hydroxide in the right-hand column that's left in this volume after compression.

At very low loadings it is a little bit low. But this is explained by the fact that the nickel itself cannot be totally compressed. Unless you have enough nickel hydroxide to fill all the little pores in the nickel when you compress it, you won't get a good value. But as you get up about three cycles, you find that you end up with about 1.6 or very close to that as the density of nickel hydroxide in all of these.

A couple of the ones, say ten impregnation cycles was a little low, nine, but I had a considerable amount of shedding from these on forming, and this would be explained by the fact that when you have the shedding, some of the nickel metal falls off, too. So you get an erroneous result. Especially the last; we had a very low result, but we have none that are higher than 1.6, really. We don't have any 1.9s, or anything like that.

So it suggests that the nickel hydroxide – the density of the actual working material when it is wet and is hydrated and whatever – probably has potassium in it and everything else, that comes to about 1.6.

(Figure 5-65)

I have done the same in the early days of electrochemical impregnation. It was done at room temperature and all, so it is not exactly the same thing that we are doing now. But we end up with the same results; that the nickel hydroxide is in there working at about 1.6 grams per cubic centimeter.

(Figure 5-66)

This is reprinted from some work that Puglisi presented in 1976 at this workshop. And we see that this percent utilization as a function of loading level shows a very sharp break at 1.6, which indicates that yes, indeed, there is something about this kind of loading. If you load at higher than that, which you can do, vacuum impregnation, you are loading in nickel hydroxide with a density of approximately 3.6.

It will go in there, but when you try to work the material, it will either not work and give you poor utilization, or if it actually is activated, it tends to swell up and the plate expands until the nickel hydroxide that is there is now 1.6 again.

This was all done at room temperature, so I have no idea as to what happens at higher or lower temperatures. If this is actually a hydrated nickel hydroxide and has four waters or six waters or something of hydration, at lower temperatures it might have a different structure, such as eight waters or two waters; or at high temperature it might. If this were done at higher or lower temperature, you might find the density is different.

This is all I have, but it is very straightforward and simple, it indicates that actual working nickel hydroxide is only 1.6 grams per cubic centimeter.

DISCUSSION

ROGERS: I don't know if I understand this correctly, but it would seem that when you compress the electrodes, you get down to a point where you cannot get ion flow through the electrolyte.

McHENRY: No. I presume in a porous electrode, in the very beginning, that you would need some way for the ions to get into the active material to make it function. And as you compress the electrode, you shut these pores down and you would find that your capacity fell off. But, in fact, it did not happen.

ROGERS: I don't quite agree with that. I think as you compress, you get very tiny pores where your capillary forces oppose your compression, and you would have, admittedly extremely small pores. But I would think they would remain open.

McHENRY: Well, what it came to was 32,000 pounds per square inch.

ROGERS: *Pretty small holes.*

McHENRY: You would think it would have some effect. You wouldn't think the capacity would increase. How small does the pore have to be?

ROGERS: *It would be hard to estimate quantitatively.*

DUNLOP: Do you conclude from this that you should compress your electrodes – when you get done you should lower them and compress them?

McHENRY: No, I am not suggesting you should do that.

DUNLOP: Why wouldn't you, though, based on the results? Why wouldn't you just compress your electrodes down? That way you would have an electrode structure when you are all done which is basically as thin as you are going to make it, and it is not going to change your performance.

McHENRY: I am not sure what would happen after many cycles. It might have an effect on the strength. As you compress them, you are going to bend all the little contact points, and will put a stress on them. Possibly they will corrode faster.

DUNLOP: I thought we could compress from the plaque – I thought you could compress without doing much damage to them.

McHENRY: I don't know. I have never run them for any length of time. I am not suggesting this is a way to make them. I am suggesting you cannot fit more than 1.6 grams per cubic centimeter in there and have it function well without swelling.

SLIFER: I have a question about the compression. You didn't mention anything about polarization.

Did you have an increase of polarization when you compressed in the electrode during the discharge of the positive electrode when they were very compressed and essentially had no voids? What polarization did you have?

McHENRY: I didn't measure this accurately, but there was no obvious change in the voltage, discharge, and charge voltages.

SLIFER: In the discharge voltages?

McHENRY: I didn't really look close into that. I was more interested in the capacity. But there might have been some, but not marked.

RITTERMAN: This is sort of a corollary to Dr. Slifer's question. But I would suspect that the compression might have decreased the surface area and resulted in an increase in overload or polarization.

Did you look into the effects of the active surface area after that?

McHENRY: No, I didn't. I just looked at the volume.

RITTERMAN: Again, you did not notice any sort of change in voltage or loss of capacity at a high current of discharge?

McHENRY: No. I was running these things at 200 milliamperes, 230-milliamperere hour electrodes. So I am running about the C rate. I didn't see any noticeable change. I didn't really measure and study the thing to make sure. But it wasn't obvious anyway.

GROSS: The density of charge and discharge in nickel epoxy hydroxide is different, so you can expect volumetric changes in that material, which of course has been observed. Now, you compressed yours in the discharge state?

McHENRY: In the charge state.

GROSS: Oh, in the charge state. So when you discharged then, you had a shrinkage?

McHENRY: I imagine that was true. But I think Dean disagrees with it. Apparently some of the data he has suggests that it expands as you are discharging. I had always thought it expands in the charging. But possibly that is not true. Maybe it is more voluminous in the discharge state.

GROSS: If you discharged it and it swelled, since you had essentially no void volume in it, the plate either would have to expand or you would be unable to discharge it.

McHENRY: They did show a little bit of springback on cycling.

(Slide)

After cycling, it did spring back a little bit. That was after about 10 or 15 cycles on this particular electrode. So it is possible that it is a little bigger when discharged. Maybe Dean is seeing a temperature effect.

LANDER: In partial answer to Jim Dunlop's question, on a program we had a few years back, we said "why don't we compress these positive electrodes and thereby gain some volume advantage and maybe a little bit of weight advantage." And we did. After a few cycles, they sprung right back to where they were, so it didn't make any difference anyway.

FOUGERE: Have you run many cycles on such compressed plates to determine the mechanical diameter after many cycles? Is it still rigid plates?

McHENRY: Yes. I have run them about 50 cycles after compression, and they still remain in one piece. They don't fall apart or anything like that.

FOUGERE: They don't perform or make any vibration or something like that on the plates?

McHENRY: No. They seem in good shape. No apparent difficulties.

GASTON: What happens now if I add some antipolar matter to the active material?

McHENRY: I didn't do that at all, so I have no idea what happened there.

SCOTT: I would like to ask John Lander what the volumetric loading was of those plates that he saw expand after he compressed them?

LANDER: I cannot give you anything but an off-the-top-of-the-skull answer there, because I don't remember the data that well, but I think it was more or less a standard loading for aircraft, standard plates which we were working on.

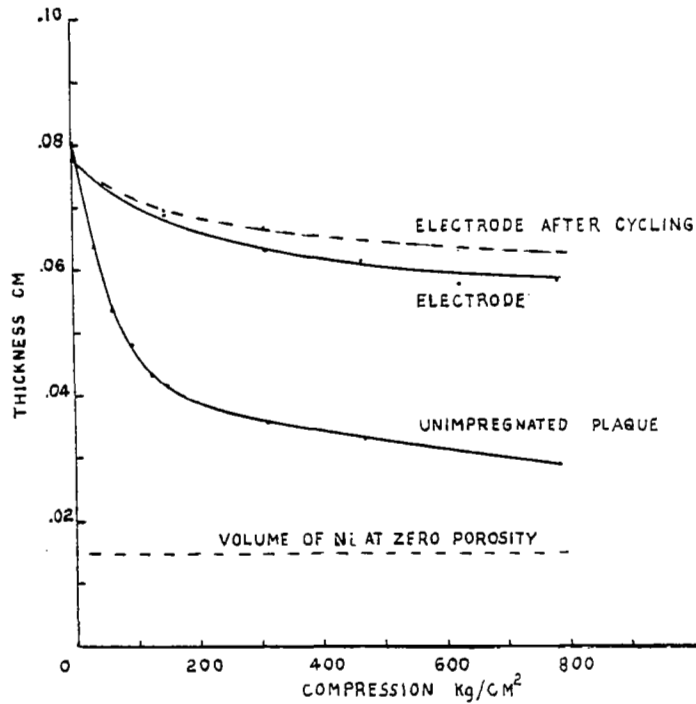


Figure 5-62

TABLE I

COMPRESSION OF ELECTRODE #2241

Uncompressed	
Weight Ni(OH) ₂	0.7402 g
Weight Ni Substrate	1.6554 g
Thickness	0.0798 cm
Theo. Cap.	0.214 Ah
Meas. Cap.	0.173 Ah
After 780 kg/cm ² Compression	
Thickness	0.0490 cm
After 6 (charge-discharge) Cycles	
Thickness	0.0528 cm
Capacity	0.190 Ah
After Second 780 kg/cm ² Compression	
Thickness	0.0480 cm
After 12 Cycles	
Thickness	0.0528 cm
Capacity	0.225 Ah
After 2000 kg/cm ² Compression	
Thickness	0.0404 cm
After 18 Cycles	
Thickness	0.0483 cm
Capacity	0.233 Ah

Figure 5-63

TABLE II
COMPRESSION OF VACUUM IMPREGNATED ELECTRODES

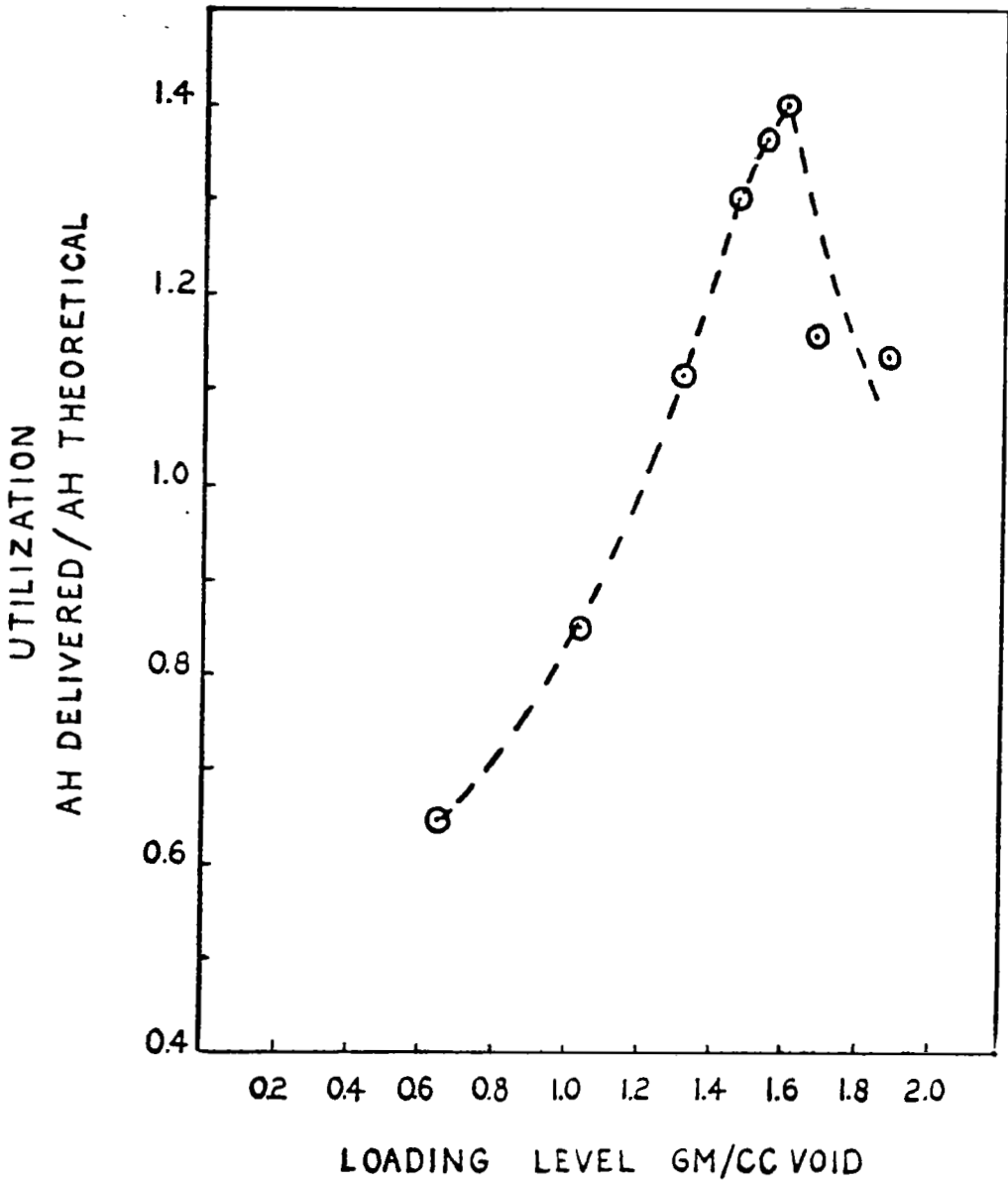
No. of Imp. Cycles	After Impregnation		After Forming		After Compression at 780 kg/cm ²			
	Thick. cm	Wt. of Ni(OH) ₂ g	Thick. cm	Wt. of Ni(OH) ₂ g	Thick. cm	Wt. of Ni(OH) ₂ g	Vol. of Ni(OH) ₂ cm ³	Density of Ni(OH) ₂ g/cm ³
1	0.0749	0.2124	0.0726	0.2213	0.0323	0.2213	0.279	0.79
2	0.0757	0.4032	0.0742	0.4112	0.0340	0.4112	0.303	1.36
3	0.0787	0.6439	0.0805	0.6659	0.0422	0.6659	0.412	1.62
4	0.0790	0.8225	0.0861	0.8421	0.0495	0.8421	0.536	1.59
5	0.0798	1.0198	0.0869	0.9283	0.0528	0.9283	0.580	1.60
6	0.0792	1.1665	0.0940	1.0835	0.0587	1.0835	0.652	1.66
7	0.0818	1.2147	0.0861	0.9878	0.0554	0.9878	0.618	1.60
8	0.0833	1.3923	0.0805	0.7597	0.0577	0.7587	0.653	1.16
9	0.0859	1.5523	0.0856	1.0132	0.0615	1.0132	0.699	1.45
10	0.0833	1.5856	0.0861	1.1053	0.0635	1.1053	0.733	1.51
11	0.0851	1.6793	0.0935	1.1097	0.0610	1.1097	0.694	1.60
12	0.0767	1.4766	0.0980	0.9163	0.0683	0.9163	0.816	1.12

Figure 5-64

TABLE III
COMPRESSION OF CATHODIC IMPREGNATED ELECTRODES

Imp. Time Min.	After Impregnation		After Forming		After Compression at 780 kg/cm ²			
	Thick. cm	Wt. of Ni(OH) ₂ g	Thick. cm	Wt. of Ni(OH) ₂ g	Thick. cm	Wt. of Ni(OH) ₂ g	Vol. of Ni(OH) ₂ cm ³	Density of Ni(OH) ₂ g/cm ³
2	0.0732	0.3044	0.0729	0.3010	0.0356	0.3010	0.312	.97
4	0.0732	0.6109	0.0714	0.5959	0.0447	0.5959	0.429	1.39
6	0.0744	0.8531	0.0744	0.8259	0.0513	0.8259	0.536	1.64
8	0.0810	1.0817	0.0818	0.9930	0.0579	0.9930	0.623	1.59
10	0.0982	1.4190	0.0859	1.1004	0.0605	1.1004	0.664	1.66
12	0.1153	1.6295	0.0851	1.0827	0.0607	1.0827	0.669	1.62

Figure 5-65



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