THE CMG NICKEL ELECTRODE

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I should like to introduce, to those of you who are not already aware of it, a new nickel electrode called the Controlled Microgeometry (CMG) electrode. It is a product of battery research at Inco's European Research and Development Center in Brimingham, UK. It has been developed to the stage of small scale production and, since early this year, has been commercially available from MPD Technololgy both in Europe and the U.S. MPD Technology is the company set up by Inco to commercialize new products resulting from research and development.

In this presentation I first want to describe the concept of the CMG electrode and its advantages over the more conventional type of electrode, and then to present some results that we have achieved with CMG electrodes in nickel cadmium cells.

(Figure 18-1)

Figure 18-1 shows diagramatically the construction of the CMG electrode. The basic element is very thin perforated nickel foil. The perforations in the foil are both accurate and regular. Each foil is coated either on one side or both sides with a layer of nickel hydroxide active material, leaving the holes clear. An electrode is produced by stacking foils together, usually 20-100 foils, so that all the small holes are in register. There is thus a sandwich-like construction of foil/active mass/foil, with cylindrical channels passing through the electrodes.

The next two figures show actual electrodes.

(Figure 18-2)

Figure 18-2 shows an ordinary view of a CHG electrode.

(Figure 18-3)

Figure 18-3 shows an expanded view. There are two different patterns of holes; their significance will appear later.

It is important to get a feel for some of the numbers involved. Typical values for the critical dimensions of the electrode are as follows: the foil thickness is about 4 m; the active mass thickness is 60 m, about 15 times the foil thickness; the hole diameter is about 0.5mm, the edge-to-edge hole spacing is about 0.75mm; the average perforated area is 15%, and the electrode thickness ia about 3mm.

(Table 18-1)

Table 18-1 shows the characteristics of a typical electrode that we are currently producing. The important thing to note is the ratio of active mass to foil, which is something over 2.5:1.

One advantage of such a construction that will have been obvious from Table 18-1 is a higher number of ampere hours per kilogram. A typical specific capacity for a CMG electrode is 190A h/kg and 350A h/l. The best figures obtained to date are 220A h/kg and 450A h/l. I think you will agree that 140A h/kg and 450A h/l would represent a fairly good sintered electrode. The main reason for this improvement is that we are using this very thin nickel foil substrate, which combines low weight with good strength and conductivity. Whereas a typical ratio for a medium loaded sintered electrode may be equal weights of active mass to support, we have a ratio of between 2:1 and 3:1.

The second advantage of this construction is really what led to the coining of the name "controlled microgeometry." All the parameters that control the performance of the electrode (the size of the holes, the distance between the holes, thickness of the foil, thickness of the active mass, the porosity and composition of the active mass) can be individually controlled over a wide range. Therefore, the electrode may be designed to give the optimum performance for a given duty cycle. The purpose of the design may be high energy density or high rate performance. To illustrate this, Figure 18-4 shows the effect of changing the pattern of holes.

(Figure 18-4)

Two 24A h electrodes are shown. In one, the area of holes is 13%. In the second it is 20%. When the electrodes are discharged at the C/5 rate, there is little difference between the two electrodes, as shown by curves 1 and 2. However, when the discharge rate is increased to the 2C rate, then the electrode with the finer 20% hole pattern shows a marked improvement both in capacity and discharge voltage.

Figure 18-4 just shows the effect of two different hole patterns. When you consider that we can vary the hole area from 5 to 45% and the hole diameter from 0.4 to 1mm, I think you will appreciate that we have scope to design for widely different discharge profiles. In fact, the examination and optimization of this aspect of electrode design is the subject of a Department of Energy contract that has recently been awarded to the Inco R&D center.

The third significant advantage of CMG electrodes is the ability to make them over a wide thickness range. Conventional electrodes are usually limited either by practical or by economic

considerations to a thickness range of about 0.5-3 mm. CMG electrodes may be made by using just a few foils, or up to about 140 foils to give an electrode 6mm thick. We have an electrode that is 36mm thick, 15cm by 30cm, with a capacity of just over 100A h for a single electrode. Thick electrodes have obvious benefits for high energy density moderate rate batteries, whereas the ability to make an electrode, say, 0.2mm thick combined with optimization of hole pattern offers the scope for very high discharge rates, in the 100 C range.

So much for the idea. Does it work?

During the research and development work on this electrode, we have made and tested several thousand electrodes, and the properties I have quoted so far are based on test results of many hundreds of electrodes. However, tests on single electrodes are of limited interest, and so I should now like to show some results achieved in cells. I shall concentrate on nickel cadmium cells, since I believe they are of most interest to this audience; however, the electrodes can and are being used in both nickel iron and nickel zinc systems.

The next few figures show the results of laboratory tests in nickel cadmium cells using CMG nickel electrodes and commercially available sintered cadmium electrodes. These results were first published in a paper presented by Dr. Turner from the Inco Research Labs at the recent Power Sources Symposium in Brighton.

(Table 18-2)

Three cells were built, and the constructions are shown in Table 18-2. The CMG electrodes varied in thickness from 0.67mm to just under 2mm. The cadmium electrodes were either 0.6 or 0.8 mm thick, and we used a number of different separator systems and two electrolyte concentrations.

Figure 18-5 shows the first few cycles of these cells.

(Figure 18-5)

All three cells require about ten cycles to reach full capacity, but a substantial portion of the capacity is available after five cycles. Cell A stablized at 111% of theoretical capacity after 12 cycles. Cells B and C leveled out at about 90% of theoretical capacity after about 15 cycles. One of the differences between cell A and the other two is the electrolyte concentration, which was 30% in cell A and 20% in the other two. At cycle 26 in cell C, the electrolyte was changed to 30% KOH, and the capacity rose to 100% of theoretical.

The formation of these cells was done in excess electrolytes. The cells were cycled without a bottom on the case, in about 20 liters of electrolyte. After cycling in this way for about 50 cycles, the cells were removed from the tank and bottoms were fixed to them. The electrolyte volume was then 3-7cm^3 A h.

(Figure 18-6)

Figure 18-6 shows the next 40 cycles of cell A. Initially the cell showed a marked fall in capacity. This highlights an important factor in the use of CMG electrodes. It is necessary with these electrodes to provide sufficient support to the electrode to prevent swelling. For the first few cycles of this cell, the plastic cell case was unrestrained and the cell case wall bulged. At cycle 70 the cell was clamped back to its original dimensions and see the capacity recovered, showing that this loss was not permanent. It is therefore very important, in the design of cells using CMG electrodes, to ensure that sufficient pressure is exerted to maintain the electrodes within their original dimensions. This can be done by designing the cell and battery stack to be close packed and providing the necessary clamping from the battery box. Alternatively -- and clamping is not possible in all cells -- for a freestanding electrode, the separator and electrode may be stitched at regular intervals. A little energy density is lost, but for some applications this approach is most appropriate.

(Figure 18-7)

Figure 18-7 shows the performance of the cell at different discharge rates. At 50% of theoretical capacity (132A h) the cell voltage at 40A drain is 1.26V, falling to 1.21V for 160A drain. The delivered capacity at 40A was 220, falling to 200A h at 160A.

(Figure 18-8)

Figure 18-8 shows the charge acceptance of one of these cells. The upper curve shows the discharge capacity expressed in both ampere hours and ampere hours per kilogram versus the charge capacity. The lower curve shows charge capacity versus charge factor. To maintain a capacity of 120A h, a charge factor of 1.03 is necessary, whereas to maintain 140A h a charge factor of 1.16 is required. Conversely, if a specific battery application requires a maximum overcharge of, say, 10% then the design parameters for this cell should include the value of 155A h/kg for CMG nickel electrodes of this particular construction.

That is a quick survey of the sort of properties that we have achieved. I shall summarize them in the next two tables.

(Table 18-3)

Table 18-3 shows the electrode properties (a) in excess electrolytes, (b)when the electrolyte was restricted to 3 - 7 cm^3/Ah, and (c) after 300 deep discharge cycles (by which I mean 100% depth of discharge every cycle), after which the capacity of the nickel electrodes is 160A h/kg and 320A h/l.

(Table 18-4)

Utilization of the nickel hydroxide is 85 - 90% after deep cycling for nearly 300 cycles, as shown in Table 18-4.

I hope I have managed to arouse your interest in this electrode, and that you may see possible applications in the aerospace field.

DISCUSSION

SENDERAK: What are the maximum discharge rates that you can get out of this type of electrode?

GUTRIDGE: You can design this electrode for very high rate applications. The standard electrode that we make (15mm thick, 15 by 30), can easily be cycled between C/1 and C/3 rates. However, with a higher area of holes and the right hole pattern, you can make a thin electrode with fewer holes in it, which can be discharged at 15 - 100 C. Thus, you design to determine the internal resistance of the electrode, and you have control over all the critical numbers that you need to design to do that.

SENDERAK: Would you cycle these cells as vented or sealed?

GUTRIDGE: The results I just described were in vented cells.

LIM: I have a related question about the rate and the amount of the electrolyte. I am not sure whether I missed something. Can you comment about the amount of the electrolyte and the rate capability? I am asking the question because you have relatively large holes, and if you are running the cell in start the condition, there would be a rather thin electrolyte connection between the active material and the separator area.

GUTRIDGE: The numbers I gave were between 3 and 7cm^3/A h of electrolyte in these vented cells. As far as the discharge rate in these cells was concerned, we went to the 2 cm^3 rate, and we were already starting to have problems with the cadmium electrode. Therefore, we were restricted by that in the rates at which we could discharge the cells.

As far as the volume of electrolyte is concerned, the porosity of the active mass is quite high. We essentially have sufficient electrolyte within the confines of the electrode to discharge or to cycle this electrode at moderate rates.

ROGERS: Am I right in thinking that the active material is packed between the sheets?

GUTRIDGE: Yes.

ROGERS: In that case, as you mentioned, you get a pressure exerted during expansion of the active materials. What pressure are we talking about? Is it sufficient, for example, to flatten the usual polypropylene or felted nylon separator?

GUTRIDGE: Let me make a comment before I answer the question about expansion. We are not looking at something that will destroy the strucutre of the electrode. However, the problem you may get is the one you mentioned. If you do not restrict the dimensions, you can put pressure on other parts of the cell.

We defined a pressure which we pressed the electrodes before we start cycling at something like $1.38 - 2.76 \times 10^4 N/m^2$ (2 - 4psi). We do not have figures for the pressure that is likely to develop in a particular cell arrangement. That depends on the design of the cell. We try and keep the electrode within its dimensions and prevent the swelling, rather than let it swell and see what happens to the cell.

ROGERS: If you do restrict it in, say, battery design as we do in an aerospace battery, then if the electrode swells the separator material is going to flatten out and you are not going to have a separator any more, you are going to have almost a solid sheet. It is an extreme case.

GUTRIDGE: We have not seen that sort of problem. One of the cells that I have described had only two layers of four-mil felted nylon. That was the only separator material. That cell performed quite satisfactorily.

BOWERS: For battery C, did the replacement electrolyte contain lithium hydroxide?

GUTRIDGE: Yes.

BOWERS: Have you discharged cells without lithium hydroxide additive?

GUTRIDGE: We have. We find that the number of cycles for formation is greater if lithium hydroxide is not present.

LEAR: Table 18-3 up there showed 300 cycles. Did you continue cycle testing?

GUTRIDGE: Yes, these cells are still being cycled, and they are up to 400, 450 cycles now.

MAURER: The figures raised a lot of interest to those of us who were involved in those previous three papers. In Figure 18-6, where you showed the capacity fading with cycling, you said that was a result of the cell bulging; then you had to squeeze it down and the capacity went back up. Why was it bulging? Was it because the active material was falling on the surface and causing an increase of thickness, and then you squeeze it back so that the resistance goes down?

GUTRIDGE: The active mass was growing. It was not actually falling off the structure, because we were able to get the capacity back, but you would finish up with a much lower density electrode if you did not hold it together.

MAURER: Then the active mass is actually increasing and you are able to squeeze it back?

GUTRIDGE: Yes. If you were to continually cycle without having some applied pressure, you would start to lose active mass. However, that was not what we observed in that short time, because we were able to get the capacity back.

GARLOCK: Have you done any temperature work with this new electrode?

GUTRIDGE: All our tests have so far been done at room temperature.

FRITTS: I was wondering if you found any problems with severe overcharge, oxygen pressure between the layers?

GUTRIDGE: No. In fact, the overcharge that we have used in a lot of our cycling tests is probably a lot higher than you would choose to use in other electrodes. We have cycled electrodes at 60, 70% overcharge continually in our early experiments. The overcharge that we use now is a standard, 30% overcharge. High overcharge is no problem.

BOGNER: How did you deposit the active material, and did it contain an additive like cobalt?

GUTRIDGE: It is deposited by a slurry coating method. Yes, it does contain cobalt.

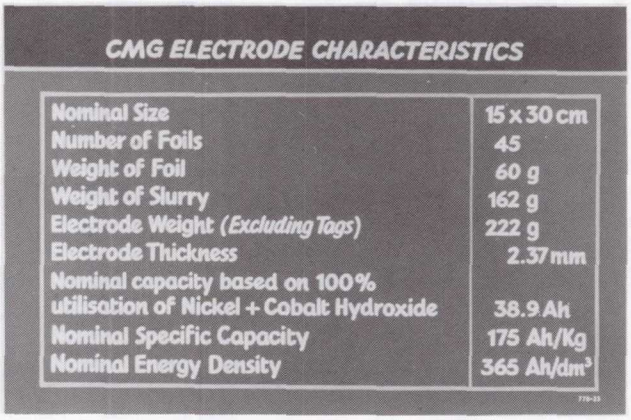

Table 18-1

	Nickel Electrodes	Cadmium Electrodes	Separator	Electrolyte
Cell A	15 electrodes 15cm x 20cm x 1mm Total Theoretical Ah = 151	15 electrodes 15cm x 20cm x 0.8mm Total Theoretical Ah = 180	Felted nylon + Polypropylene Mesh	30% KOH + Li HO
Cell B	25 electrodes 15cm x 30cm x 0.67mm Total Theoretical Ah = 264	25 electrodes 15cm x 30cm x 0.6mm Total Theoretical Ah = 300	Felted nylon	20% KOH + Li HO
Cell C	10 electrodes 15cm x 20cm x 1.96mm Total Theoretical Ah = 212	20 electrodes 15cm x 20cm x 0.8mm Total Theoretical Ah = 240	Felted nylon + Polypropylene Mesh + Cellophane	20% KOH + Li HO

Table 18-2

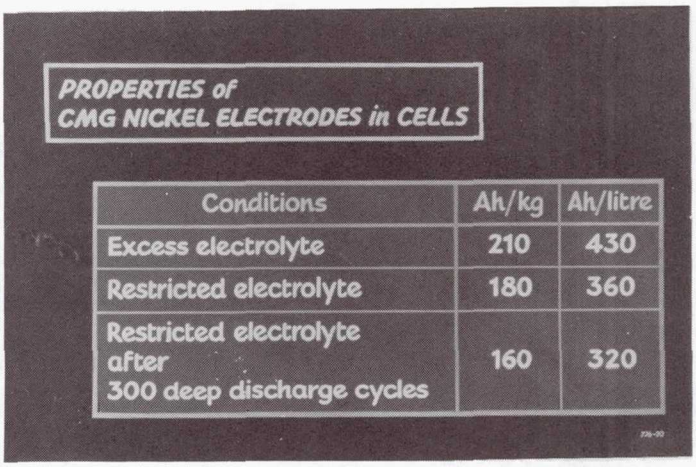

Table 18-3

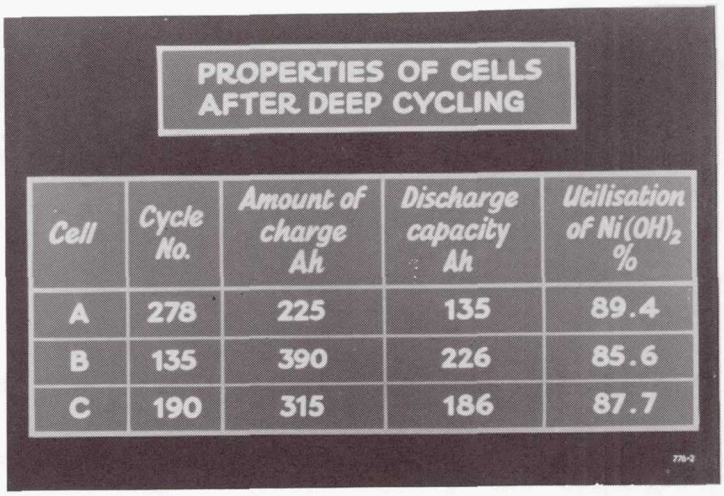

Table 18-4

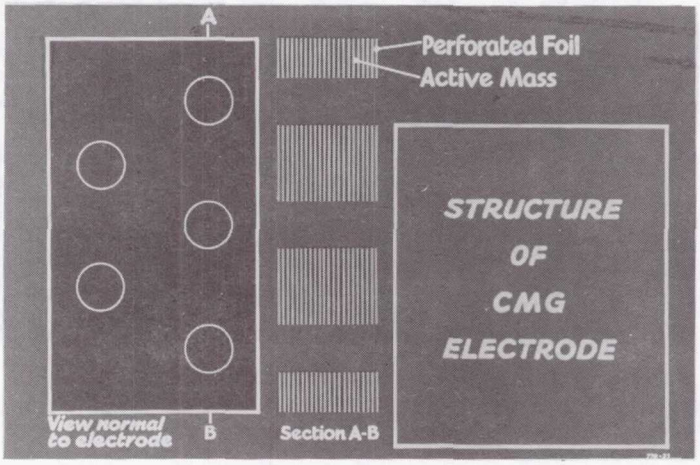

Figure 18-1

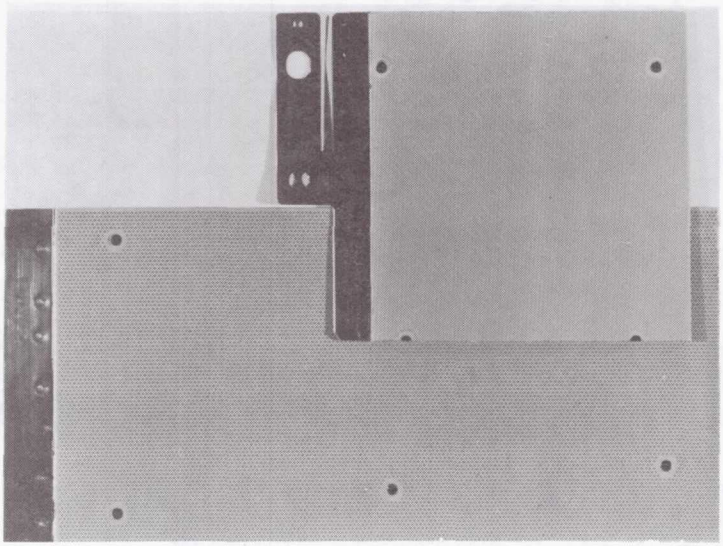

Figure 18-2

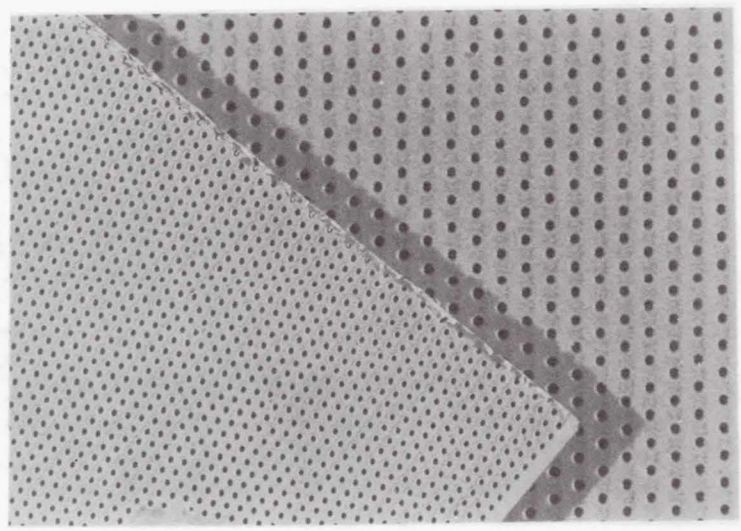

Figure 18-3

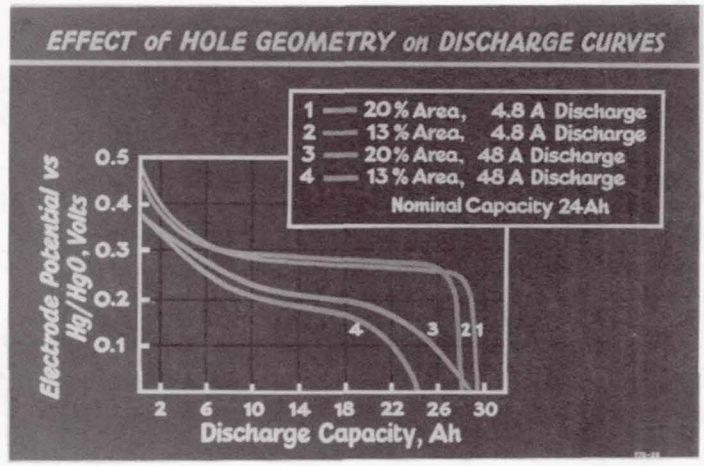

Figure 18-4

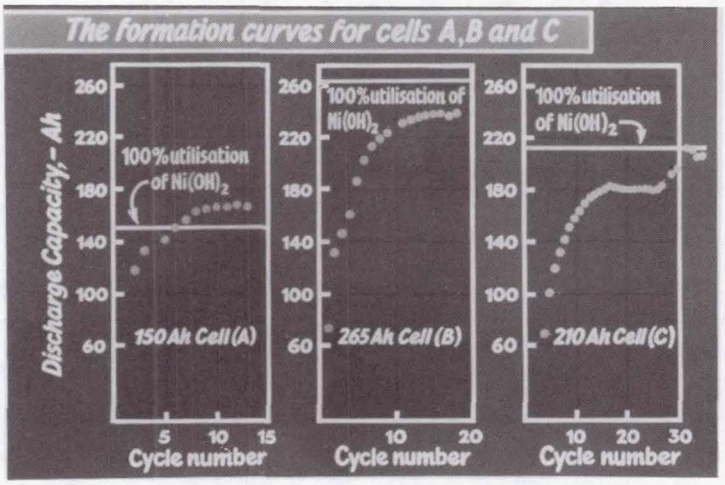

Figure 18-5

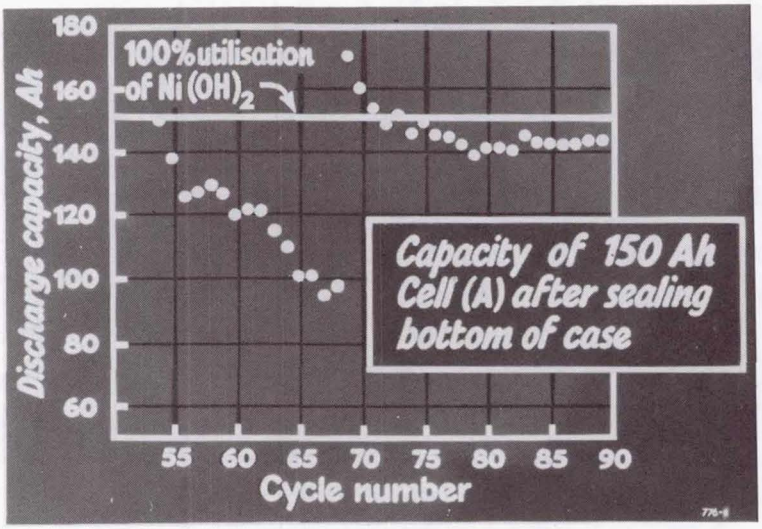

Figure 18-6

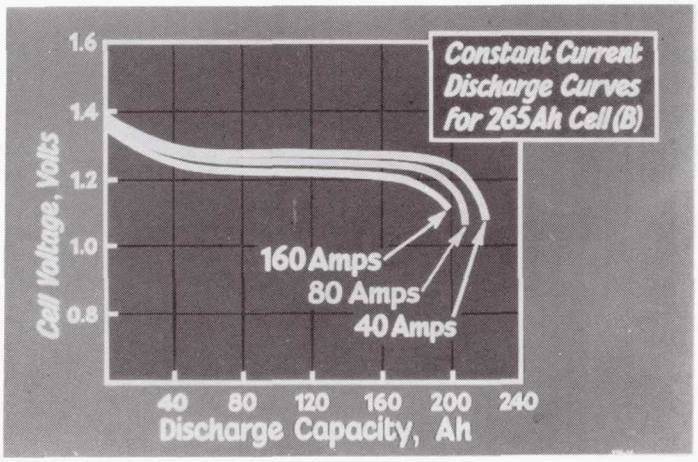

Figure 18-7

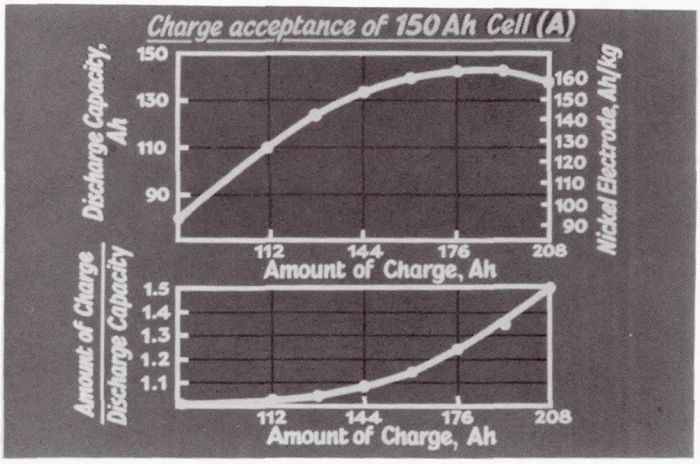

Figure 18-8