Corrosion as a process determining the efficiency of porous nickel plates impregnated with nickel hydroxide

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The methods used for the impregnation of porous nickel plates in alkaline batteries are compared. The effect of the corrosion process on these plates in terms of the efficiency, capacity and life of nickel–cadmium batteries with sintered electrodes is examined.

1. Introduction

The introduction of electrochemically active substances into the pores of plates sintered from nickel powders, i.e., impregnation with nickel hydroxide or cadmium hydroxide, has been described in detail by Fleischer [1]. The method consists of impregnating the plates in hot, concentrated nickel or cadmium nitrate solution for a short period. The impregnated nickel plates are then placed in an electrolyser and connected to the negative pole. The electric circuit is closed by pouring a hot solution of KOH into the electrolyser. After a short cathodic polarization with a current of high density (5–10 A dm^{-2}) the plates are taken out, washed and dried. Such an impregnation cycle is repeated about a dozen times in order to fill the porous plates fully with hydroxides.

During the last twenty years other methods for the impregnation of porous plates have been developed [2, 3]:

(a) The chemical method. This consists of lengthy immersion (from 2–24 hours) of porous plates in concentrated hot nickel salt or cadmium salt solution, precipitation of the appropriate hydroxides and washing and drying the plates. The use of higher temperature, vacuum and change of pH or solution density results in the shortening of the immersion time or in the lowering of the number of impregnation cycles [4–8].

(b) The thermal method. This was developed by Casey, Bourgault and collaborators [9–11]. It involves a short immersion of the plates in molten nitrates, followed by placing the plates in an oven where thermal decomposition of the nitrates takes place. This decomposition results in the formation of basic salts in the pores, which under the action of the solution are converted into hydroxides. The plates are washed and dried and the impregnation cycle is repeated several times.

(c) The electrochemical method. This was first developed by Kandler [12] and described by Häusler [13] and Henry [14]. It consists of cathodic polarization of porous plates in not too concentrated solutions of nickel or cadmium salts. The polarization is usually started at a low current density (~ 10 mA cm^{-2}) for several hours. During polarization hydroxide deposits in the pores of these plates and after the completion of the process there is no need to place the plates in the solution. After impregnation they can be used directly, with only a slight rinsing, for the assembly of batteries.

The aim of all the above methods is a quick and easy introduction of an adequate amount of active substance into the pores of the nickel plates. The amount present usually enables positive electrodes to give at least 0.3–0.4 A h cm^{-3}, using the volume of the whole electrode, and negative electrodes to give 0.5 A h cm^{-3}. The impregnation process, and especially the immersion operation, is accompanied by a series of incidental processes which affect the capacity, life and other electrode and battery parameters.

In this paper various impregnation methods are compared and the results of corrosion of nickel plates are discussed. Special attention is devoted

to the effect of corrosion on plate properties. Only the nickel hydroxide electrode (positive electrode) is examined, because this electrode is the limiting factor for capacity, life and other properties of the nickel–cadmium battery with sintered plates. It is difficult to determine the degree and the amount of the electrode corrosion which has an influence on this plate's properties.

2. Experimental

Porous nickel plates prepared by the slurry technique in production conditions were used in these experiments. For the impregnation of porous plates with nickel hydroxide a recrystallized solution of nickel nitrate with a density of 1.74–1.78 g cm^{-3} at 105° C was used, and for the precipitation, an aqueous KOH solution with a density of 1.25 g cm^{-3}. To facilitate the evolution of hydrogen bubbles from the solution during the corrosion tests, which used the method of hydrogen volume measurement, a solution with a density of 1.60 g cm^{-3} at 80° C was used.

The measurement of electrode capacity was made in cells, in which porous plates impregnated with cadmium hydroxide were the counter electrode. In these cells unwoven polyamide fabric was used as a separator and KOH with a density of 1.25 g cm^{-3} as the electrolyte. The cells were charged for 15 hours with a charge rate $C/10$, where C is the capacity of a group of positive electrodes. Cells were discharged with discharge rate $C/2$ to the end-point voltage of 1 V on the cell terminals or to a potential of 1.56 V in relation to the ZnHg/KOH electrode.

The capacity between 4–7 cycles was taken as the electrode capacity. During cell-life tests, cycles without checking were performed using $C/2$ charge rate for two hours and $C/1$ discharge rate for one hour. The results presented are generally an average from six measurements.

3. Results and discussion

Porous plates were prepared from three different powders by a slurry technique. The nickel powders, produced by the carbonyl method, had a similar bulk density (~ 0.6 g cm^{-3}) but differed from each other in respect to particle size (see Table 1). The average size of the powder particle is a decisive factor in determining porous plate quality. Powders with smaller particles shrink more than powders composed from coarser particles during sintering. The porosity depends on powder shrinkage, therefore the bigger the diameter of powder particles, the smaller the shrinkage and the plate porosity is increased.

In order to compare the sintering quality of the three kinds of nickel powders used in this work, scanning electron microscope photographs of the porous plates (Fig. 1) were obtained. By comparing the area of the physical contact between particles with particle size, it can be seen that they are equal to or a little smaller than the particle diameter. This means that during sintering a bulk diffusion of nickel atoms is taking place and that after such sintering a strong integration of powder occurs.

The successive increase in weight of nickel hydroxide in porous plates in successive impregnation cycles is presented in Table 2. The total weight of hydroxide, its efficiency and electrode capacity obtained by various impregnation methods are also presented. Plates prepared from powder III, giving the biggest pore diameters, i.e. the best conditions for the diffusion of nickel nitrate solution into the plates, were used for the investigations.

To fill the pores completely using Fleischer's method, a large number of impregnation cycles is needed. This is shown by the comparison of data in Table 2. Using 'chemical' or 'thermal' methods the total filling of pores can be obtained after four impregnation cycles (in the fifth cycle the

Table 1. Physical properties of sintered nickel plates as a function of average powder particle size

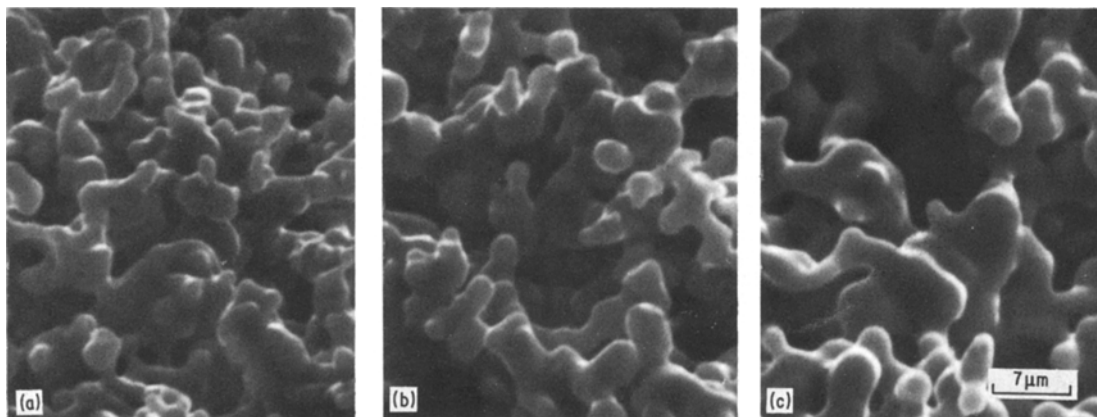| Powder designation	Average particle size (μm)	Plate porosity (%)	Resistivity (Ω mm^2 m^{-1})	Specific surface area (m^2 g^{-1})	Pore size distribution (%)		
					< 1.25 μm	1.25–7.5 μm	> 7.5 μm
I	1.4	68	0.81	0.24	27	70	3
II	2.4	72	0.91	0.22	15	50	35
III	2.8	73	1.13	0.18	13	37	50

Fig. 1. Scanning micrographs of porous sintered plates prepared from three types of nickel powder, 1750X. (a), Type I; (b), Type II; (c) Type III.

hydroxide precipitates only on the plate surface). Plates impregnated by the 'chemical' method show the highest capacity which, indeed, exceeds the theoretical value (0.30 A h g^{-1} compared to the theoretical 0.29 A h g^{-1}) assuming that, in 6 M KOH and with a low charging rate over the initial formation cycles, only phase β is formed [15]. Dissolution corrosion of the porous plate can be the only cause of this increase in weight of Ni(OH)$_2$ taking place during the impregnation operation.

The increase of nickel hydroxide in the pores of plates made from type I powder is shown in Fig. 2 (the internal surface area in these plates is most subject to corrosion) as a function of the amount of nitric acid added to the nickel nitrate solution. Nitric acid is added to the solution which is used for the first impregnation operation only. The increase of hydroxide in the plates after the first impregnation cycle and the total amount after

four cycles is inversely proportional to the quantity of nitric acid in the nickel solution. This gives rise to the dependences shown in Fig. 2. It should be noted that the increase from the second to the fourth cycle is the same for all plates. It is observed that plates immersed during the first impregnation cycle in nickel nitrate with an addition of 150 cm^3 acid solution per 1 dm^3 of impregnation solution underwent visible dis-solution and on weighing showed a loss of mass.

Whereas the capacity per gram of Ni(OH)$_2$ given by the plate (Fig. 2) is directly proportional to the amount of acid, the capacity reaches 0.38 A g^{-1} when the acid content in the nitrate is highest. Based on these results it can be con-cluded that hydroxide yield calculated from plate material increase can be an apparent parameter because of the degree of corrosion dissolution of the porous plates.

The variation in the capacity of plates as a

Table 2. Plate loading and capacity parameters

Impregnation method	Ni(OH)$_2$ specific increase in successive impregnation cycles (g cm^{-3})									Total increase (g cm^{-3})	Capacity	
	1	2	3	4	5	6	7	8	9		(A h g^{-1} Ni(OH)$_2$)	(A h cm^{-3})
Fleischer	0.21	0.19	0.15	0.13	0.13	0.09	0.08	0.10	0.06	1.14	0.26	0.29
Chemical	0.61	0.39	0.23	0.13	—	—	—	—	—	1.36	0.30	0.41
Thermal decomposition	0.48	0.40	0.19	0.18	—	—	—	—	—	1.25	0.24	0.30
Cathodic polarization*										1.25	0.23–0.28	0.30

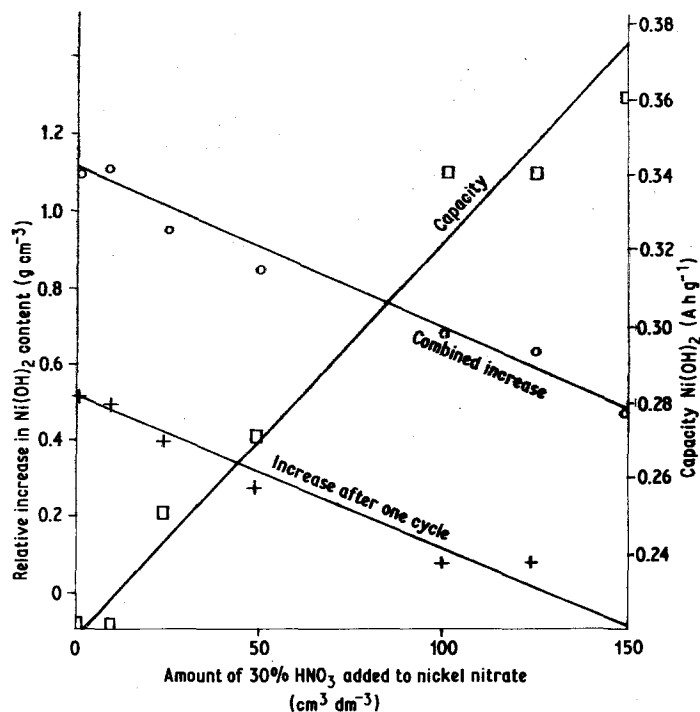* Results obtained with the cathodic polarization method will be presented later.

Fig. 2. Weight gain of $Ni(OH)_2$ and electrochemical capacity as a function of free HNO_3 content in nickel nitrate solution.

function of immersion time is presented in Table 3. The impregnation is performed in nickel nitrate solution without the addition of nitric acid. The plates are impregnated only once.

Plates made from nickel powder with the highest surface area (type I) are characterized by a high capacity $(0.4\,A\,h\,g^{-1})$ even after the shortest immersion time in acidic nickel nitrate solution, i.e. plates prepared from this powder after 15 minutes immersion undergo much corrosion. The plate capacity obtained from the two other powders immersed for 15 minutes is lower and is inversely proportional to powder particle size. Plates made of powder I impregnated for longer than 15 minutes show a lower final capacity which diminishes with increasing immersion time.

Table 3. Plate capacity $(A\,h\,g^{-1})$ as a function of immersion time in molten nickel nitrate

Immersion time (min)	Capacity for three types of nickel sinters $(A\,h\,g^{-1}\,Ni(OH)_2)$		
	I	II	III
15	0.40 ± 0.03	0.29 ± 0.01	0.27 ± 0.01
60	0.38 ± 0.02	0.31 ± 0.01	0.33 ± 0.01
240	0.36 ± 0.01	0.30 ± 0.01	0.34 ± 0.01
360	0.35 ± 0.01	0.29 ± 0.01	0.33 ± 0.01

The influence of immersion time on electrode capacity (on a weight or volume basis) is shown in Fig. 3. Results presented in the diagram refer to investigations of cells comprising plates made from powder I. Positive plates are impregnated with hydroxide using the chemical method for four cycles. Different immersion times are used in the first cycle; in the second to fourth cycles the impregnation time is 2 hours.

The data in Fig. 3 show that when the immersion time becomes longer, electrode capacity increases. The capacity per gram of $Ni(OH)_2$ reaches the highest value in plates immersed for 30 minutes, but the volumetric capacity reaches a maximum after 2 hours. After reaching maximum values, both parameters decrease together with further increase in immersion time.

The influence of the two factors on impregnation efficiency is shown by comparing data included in Table 3 and Fig. 3. On one hand the apparent yield increases as a result of corrosion, i.e. dissolution or oxidation of the porous plate. On the other hand the decrease of capacity with increased immersion time may be due to the increase in the extent of precipitated basic salts in an outer surface layer. During impregnation cycles several successive processes take place.
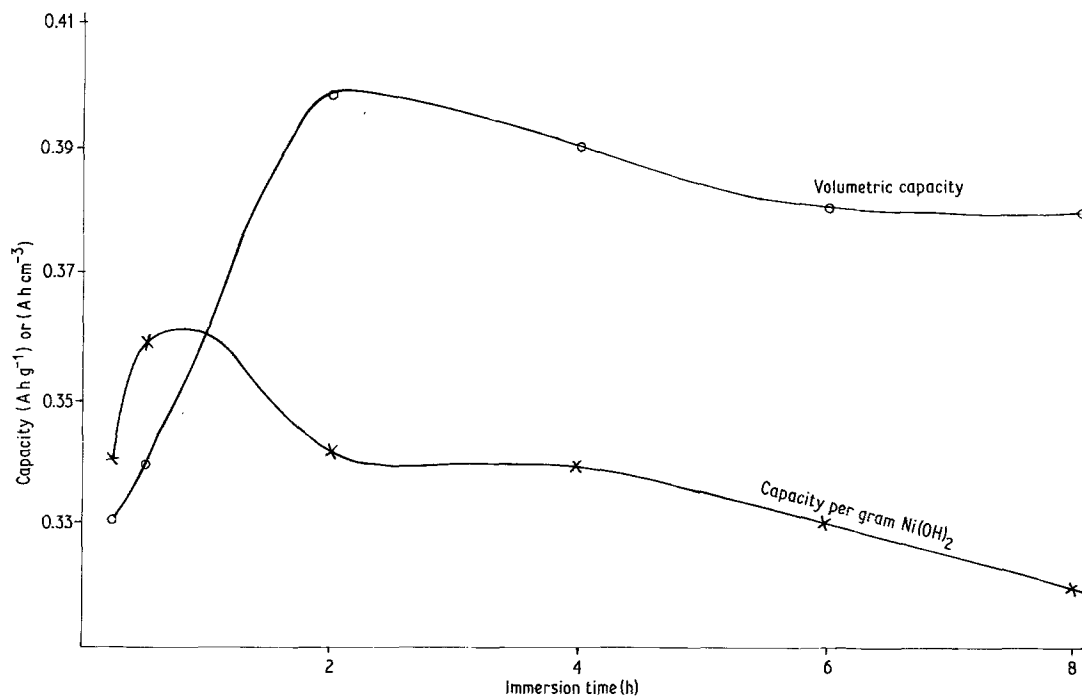
Fig. 3. Capacity expressed in terms of Ni(OH)$_2$ weight or plate volume as a function of immersion time during the first impregnation cycle.

When dry plates are placed in concentrated nitrate solution above 80° C, a rapid release of air enclosed in the pores occurs during the first minute. This phenomenon disappears after 2–4 minutes and after only 5 minutes fine bubbles of hydrogen evolve from the plate. When nitrate solution with a low pH, including free nitric acid, is used for the experiment, the solution pH increases after some minutes of impregnation. When the pH exceeds 4 grey-green deposits of basic nitrates begin to precipitate. A decreased rate of hydrogen evolution is observed as the amount of basic salt deposit rises. In the second and subsequent impregnation cycles evolution of hydrogen is not observed. These two phenomena, dissolution of the porous plate and the precipitation of basic salts, have an influence on the plate capacity. Nickel dissolution apparently influences the increase in capacity, and basic salt precipitation inhibits corrosion and at the same time encourages the blocking of the electrode outer surface with hydroxide. The growth of this hydroxide layer diminishes the possibility of uniform and rapid discharge of oxidized hydroxide which results in a drop in capacity.

For the assessment of plate corrosion the volume of hydrogen evolved as a result of porous plate dissolution was measured. The measurements were carried out using nitrate solution with a density of 1.6 g cm^{-3} at 80° C and pH = 3.5. Results showing the increase in volume of hydrogen as a function of immersion time are presented in Fig. 4. Comparing the dependences for the three types of plate, it can be seen that at the beginning the volume of hydrogen evolved is similar and independent of the kind of plate used. Differences can be observed only after immersion for 15 minutes: the finer the powder used for plate production, the greater the volume of hydrogen evolved. For plates prepared with powder I, hydrogen evolution stops after 60 minutes.

The volume of hydrogen evolved as a function of immersion time, for plates sintered from powder I at different temperatures for 10 minutes, is presented in Fig. 5. The corrosion rate is strongly influenced by sintering temperature as can be seen from the data presented. When the sintering temperature is increased the volume of hydrogen evolved decreases, i.e. the corrosion and dissolution of the porous plates diminishes, with the exception of plates sintered at 600° C which are damaged.
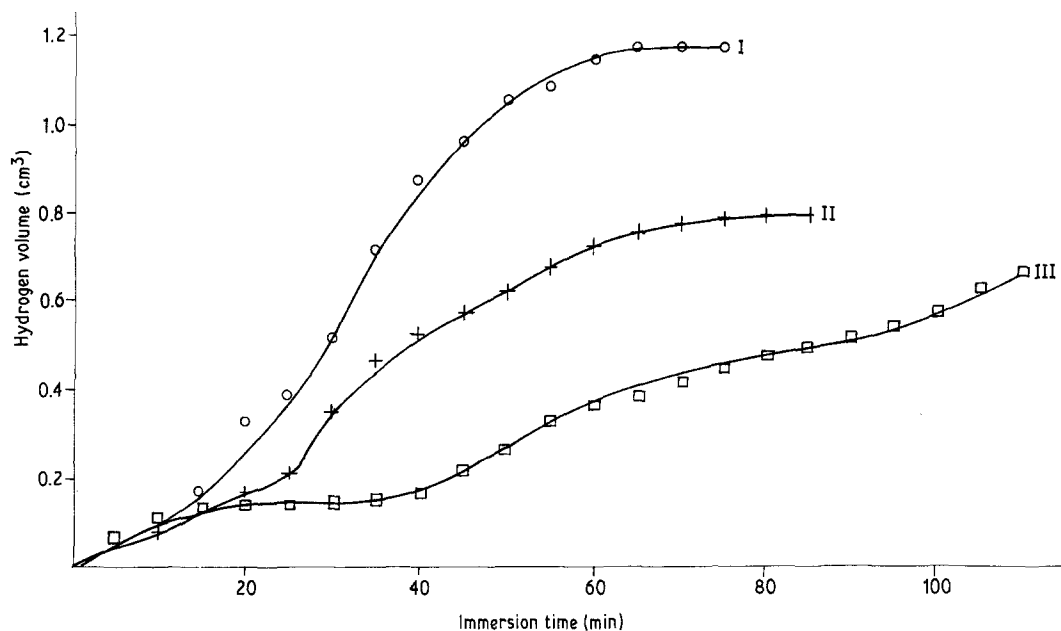
Fig. 4. Volume of hydrogen evolved during impregnation of porous plates, as a function of immersion time for the three types of porous plates.

Cell capacity as a function of the number of charge–discharge cycles is presented in Fig. 6. Cell capacity is limited by the positive electrode capacity. The particular curves represent the capacity change of positive electrodes with varying immersion time (corrosion level in per cent) in the first impregnation cycle. According to the results, electrodes immersed for 30 minutes during the first impregnation cycle show the lowest specific capacity. The capacity of these cells rises however with the increase in the number of charge–discharge cycles performed after the electrodes have been previously immersed for 6 hours during the first impregnation cycle. But the capacity of these cells decreases rapidly after 150 cycles and the cells were withdrawn from further tests after 450 cycles because of short circuiting between groups of plates. A capacity drop is also observed for electrodes which have been immersed for 2 hours during the first impregnation cycle, but only after 450 cycles. The capacity of electrodes immersed for 1 hour diminishes slightly, but not until 150 test cycles. Electrodes immersed for 30 minutes during the first impregnation cycle show at first a high, then a slow, steady capacity increase with increasing charge–discharge cycle number.

The influence of impregnation time on dis-charge capacity over 150–152 cycles, for different current values, is presented in Fig. 7. At the lowest discharge current, the capacity rises with immersion time, but at higher currents a capacity drop is observed. This drop increases when the immersion time in the first impregnation cycle becomes longer.

The behaviour of the positive plates during successive charge–discharge cycles and on dis-charge with high current points to the influence of two related factors. One of these factors is the phenomenon of nickel dissolution during the impregnation operation, which causes a difference in the initial capacity of electrodes. However, after several tens of cycles differences in the capacity are increasing, i.e. plate corrosion is growing with cycle number. This is brought about by increased oxidation of the porous nickel support of the electrode. The electrode support material after anodic oxidation provides an additional source of electrochemically active material. It is this second factor which has an influence on electrode behav-iour during cycling in cells. The anodic oxidation of the nickel support during cycling is the more severe the greater the level of corrosion of the plates during impregnation. The anodic oxidation of the electrode support in successive cell cycles results in weakening of the porous plate structure.
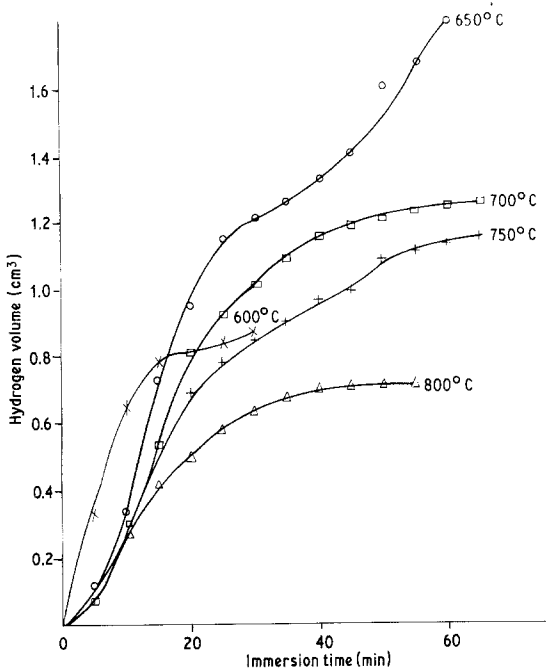
Fig. 5. Hydrogen volume evolved as a function of porous plate immersion time for different sintering temperatures.

Similarly plate dissolution leads to the destruction of contacts among particles.

The increase in plate corrosion due to anodic oxidation of the plate in successive charge–discharge cycles results in plate destruction when the plates are initially impregnated for more than
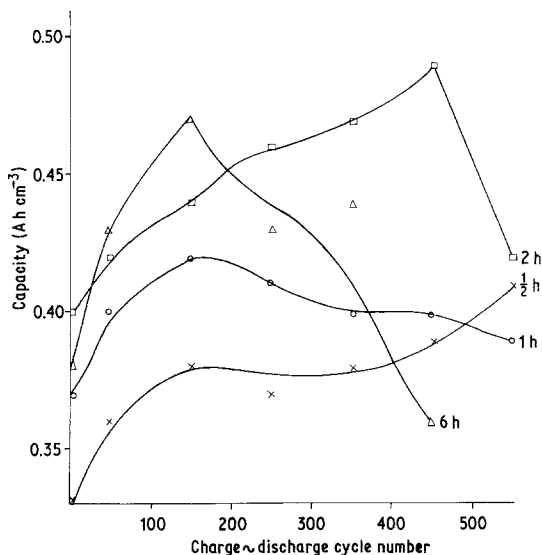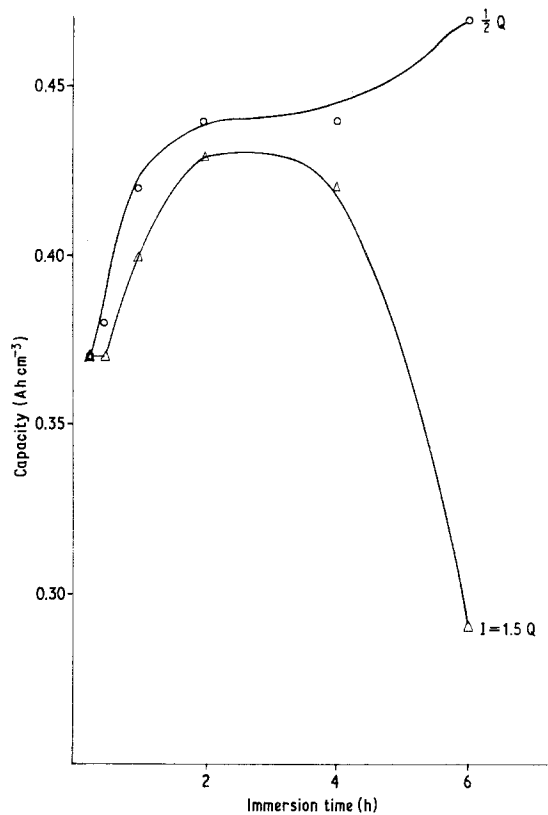

Fig. 7. Capacity (A h cm^{-3}) of electrodes as a function of immersion time during the first impregnation cycle at different values of discharge current.

4 hours. This occurs after 450 charge–discharge cycles. After 550 cycles all cells were dismantled and it was found that for electrodes impregnated for:

15 min	6 out of 9 had not failed
30 min	4 out of 9 had not failed
1 hour	1 out of 9 had not failed
2 hours	all had failed
4 hours	all had undergone a strong deformation.

The influence of anodic oxidation on seemingly compact electrodes discharged with high currents (Fig. 7) can be observed at an earlier stage, probably because during the corrosion which follows the immersion operation, the nickel forming mechanical contact between particles is being dissolved. These contacts, considering the stresses arising in them, ought to be more subject to corrosion than individual particles. During cycling, contact corrosion is increased owing to anodic oxidation. This phenomenon manifests itself in

Fig. 6. Electrode capacity (A h cm^{-3}) as a function of charge–discharge cycle number for electrodes having different immersion times in the first impregnation cycle.

the initial period of electrode cycling by an increase in resistance of the nickel support, which can be observed particularly with cells discharged with higher currents.

The negative influence of corrosion dissolution can be totally removed by using short immersion times (Fleischer's method). This, however, results in a decrease of electrode volumetric capacity and an increase in the number of impregnation cycles necessary. The thermal methods allow one to limit corrosion substantially by shortening immersion time. Similar impregnation effects are obtained by cathodic polarization in nickel nitrate with, however, an undesirable elongation of impregnation–polarization time.

A total removal of corrosion phenomenon seems to be unprofitable, because it results in electrodes with a low specific volumetric capacity (below $0.35 \, \mathrm{A\,h\,cm^{-3}}$). Therefore the choice of impregnation methods and parameters depends on one hand on the physical properties of the nickel powder used for the production of porous plates, and on the other hand on the requirements imposed by the cells (a high initial capacity or a better discharge capability with high currents and long life).

4. Conclusion

Electrodes made from plates impregnated by a chemical method, using immersion during the first cycle in a slightly acid solution, give a volumetric capacity above $0.45 \, \mathrm{A\,h\,cm^{-3}}$. However, the life of batteries with such electrodes, especially batteries with type I plates, is not satisfactory.

Nickel–cadmium batteries with positive plates impregnated by thermal decomposition methods are characterized by capacity depreciation of about 10–20%. The life of these batteries, even when type I plates are used, is twice as high as batteries with plates impregnated by the chemical method and exceeds 1500 cycles at high discharge rates.

In the case of starter batteries discharged with a current 30 times higher than the nominal capacity value, the advantageous properties of nickel–cadmium batteries sintered from fine powders (plates with low specific resistance) are confirmed. Starter batteries made with type I plates feature a 10% higher capacity than batteries with type II plates at such a discharge rate.

Acknowledgement

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