ELECTROCHEMICAL IMPREGNATION BATH AGING

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Summary

The effect of bath aging on electrochemical impregnation of nickel hydroxide is described. Bath aging is evidenced by a reduction in active material loading with bath usage. This phenomenon of bath aging was experimentally investigated by using two substantially different nickel sinter plaque types.

The data from this experiment suggest that mean pore size and pore spectrum over the range studied are not important parameters in determining bath life. For both plaque types, bath aging occurs to about the same degree. Practical limitations to plaque impregnation were found to be about 500 cm^2 per liter of bath solution for plaque of the structure used in this study.

Introduction

Dry powder plaque production techniques were developed with Inco type 255 powder. Plaque produced by these techniques, with the desired sinter porosity of 82%, has a smaller median pore size than plaques produced by most other techniques. Subsequently, nickel hydroxide deposition by an aqueous electrochemical method using a large bath revealed a bath aging phenomenon. The bath aging is characterized by a reduction in active material loading with use under constant process parameters. The question arose as to whether the uniquely smaller median volume pore diameter of the 255 plaque was related to this aging phenomenon. To aid in answering this question, dry powder plaque production techniques for Inco type 287 powder were developed. The 287 plaque produced by these techniques had the large median pore size of commercially produced plaque. These two plaque types were then used to study bath aging as a function of pore size.

Experimental

The plaque pore-size distribution was characterized by use of the mercury intrusion porosimeter. The data in Fig. 1 show pore spectra for the 255 and 287 plaques. Two items are notable. The first is that the median volume pore diameter of the 255 plaque is 8.7 μm, while that for the 287 plaque is
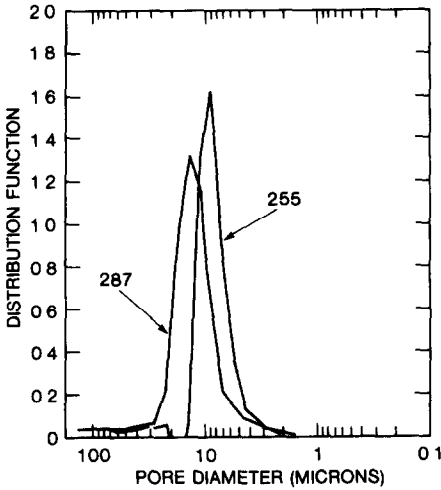
Fig 1 Pore diameter distribution for 255 and 287 dry powder plaques

TABLE 1

Plaque properties

Type	255 Plaque	287 Plaque
Density (g/cm^3)	1 71	1 51
Thickness (cm)	0 092	0 088
Plaque porosity (%)	79 7	82 2
Sinter porosity (%)	82 5	85 2
Median volume pore diameter (μm)	8 7	12 7

12.7 μm. Secondly, the pore size distribution for the 255 plaque is much narrower (7 μm *vs.* 14 μm for the middle 80 vol% of pores) than that for the 287 plaque. Table 1 lists the average plaque properties for each type.

Figure 2 displays the potted and polished cross-sectional back-scatter electron images for the 255 and 287 plaques. The potting was accomplished using Shell-Epon 815 resin with Nadic Methyl Anhydride curing agent plus BDMA catalyst under vacuum at 80 °C for 8 h. Polishing incorporated standard metallographic procedures using silicon carbide papers to diamond polishing wheels. Qualitatively, it can be seen that the 255 plaque has a much more uniform distribution pore structure. This is characterized by the lack of large voids and of the clumping of sinter particles. Further characterization of this plaque is described elsewhere [1].

These plaques are considered sufficiently different in pore spectrum to allow a determination of the effect of pore spectrum on bath aging.
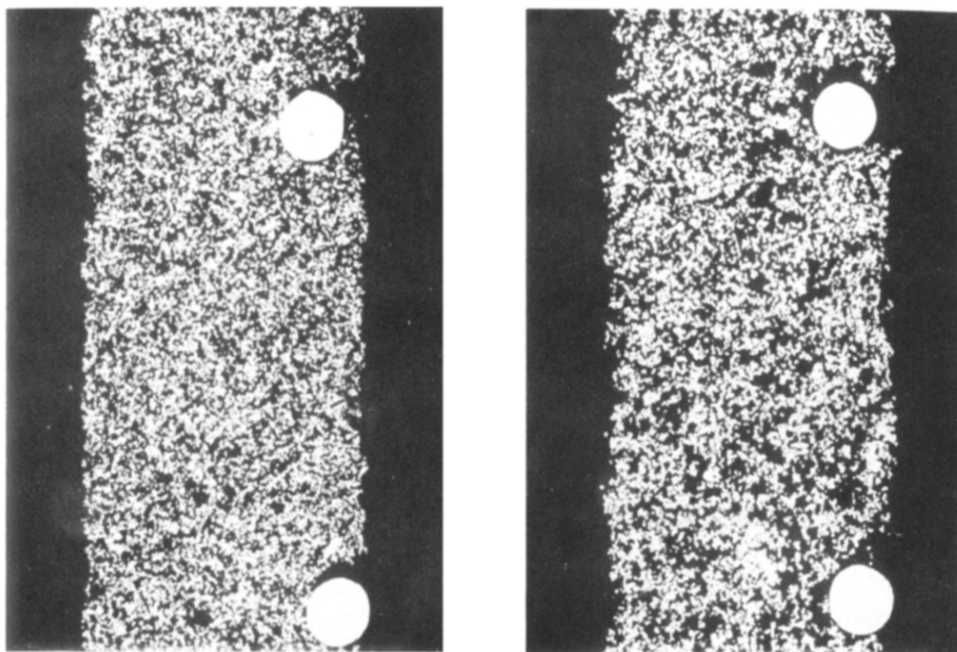
Fig 2 Cross sections of plaques made with 255 and 287 Inco powder

Some preliminary experimentation with impregnation techniques was performed with small plaque samples in beakers of impregnation solution. Using the beaker method simplifies the experiment and provides data relevant to large bath operation. Data obtained using the beaker method show reasonably good correlation with large bath data.

Uniformly-sized plaque samples of the same type were sequentially impregnated with nickel hydroxide in the same fixed quantity of solution. Controlled corrections were made to the solution concentration in accordance with the Bell Labs. impregnation procedure [2, 3]. Furthermore, two beaker solutions were required: one for the 255 type and one for the 287 type. The experiment was performed such that only the plaque type was variable. Therefore, all operations, such as plaque preparation, impregnation, formation, washing, drying, and cycling were carried out similarly for all samples. Specifically, two separate, but identical, one liter electrolyte solutions were prepared, one for each plaque type. Each electrolyte consisted of 1.5M nickel nitrate, 0.0075M cobalt nitrate, and 0.075M sodium nitrite made acidic (pH 3.0 - 3.5) by the addition of nitric acid.

Following each impregnation, the solutions were adjusted by additions, to maintain these concentrations.

The two sample types were impregnated in separate reaction vessels, which consisted of two-liter beakers each containing one liter of the electrolyte solution, a Teflon sample holder, and two electrically connected

7.6 cm × 15.2 cm expanded-mesh platinized-titanium anodes. The impregnations were carried out at a temperature of 95 °C.

Each pair of plaque samples (consisting of one 255 and one 287 type) was impregnated in series at a current density of 0.08 A/cm² for 60 min. During the impregnations, sodium nitrite (1.0 - 1.5M) solution was added to maintain a nitrite ion concentration of 0.075M. This operation required the addition of 0.08 mole of NaNO₂ for each impregnation, and was added by buretting 13 equal portions at 5 min intervals. Following impregnation, the samples were rinsed and allowed to soak in deionized water for 30 min.

Formation cycling was carried out in 30 wt.% KOH at a temperature of 60 °C. A complete formation cycle consisted of 14 min periods of charge, discharge, and recharge at a current density of 0.25 A/cm², followed by a final discharge at a current density of 0.17 A/cm² until the sample gassed. Pairs of samples were formed in series against nickel sheet counter electrodes with fresh electrolyte for each sample.

Following formation, the samples were passed several times through a deionized water brush scrubber. Then they were thoroughly washed and dried at a temperature of 60 °C for 30 min. Finally, the samples were cooled in a desiccator cabinet and then weighed.

Results

An initial measure of active material loading is the weight gained by the plaque during impregnation. Figure 3 shows weight gain normalized for plaque weight *vs* number of runs. Since a run represents a one-sided area of
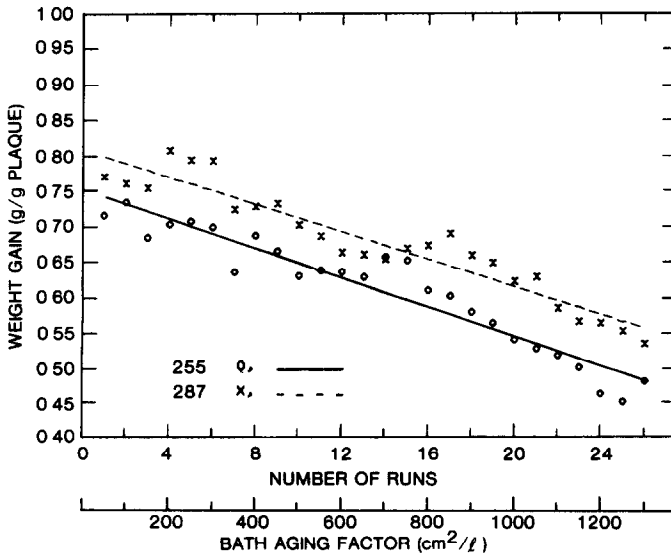

Fig 3 Normalized weight gain *vs* bath life for 255 and 287 dry powder plaques
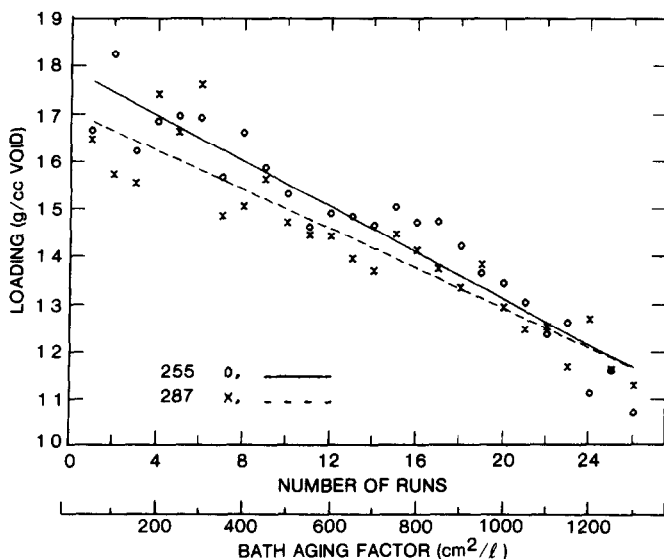
Fig 4 Active material loaded into void volume *vs* bath life for 255 and 287 dry powder plaques

approximately 50 cm² of plaque per liter of solution, the data are also shown as a function of cumulative cm²/l, defined as the "bath aging factor". The straight line representations are obtained by linear regression. In general, the 287 plaque had slightly higher normalized weight gain than did the 255 plaque. The data for both plaque types exhibit the bath aging effect to about the same degree. Figure 4 displays the same data in the common form of grams of active material loading per cubic centimeter of void volume. Typical loading specifications for $Ni(OH)_2$ electrodes are 1.6 ± 0.1 g/cm³. Under the restricted conditions for this experiment, loading thus specified is achieved for only about 8 - 10 runs. Therefore, 400 - 500 cm²/l could be impregnated before loading would fall outside the specification. This can be expressed as cumulative weight gain per liter; *i e*, 45 - 60 g/l.

Formation capacity is another indication of extent of bath aging. Figure 5 displays data pertaining to the formation capacity of both plaques. The results are quite similar to those pertaining to weight gain and loading, as might be expected. Formation capacity is measured at very high rates (5 *C*) by observation of the onset of gassing during discharge. A more accurate and useful measure of capacity is produced by flooded measurements at lower (*C/2*) rates. Figure 6 shows that this flooded capacity measurement is approximately 18% greater than formation capacities for the initial runs, but only 8% greater for the later runs. The average utilization of the active nickel species, assuming one electron transfer, is very nearly 115% for both plaque types at this point. When this capacity cycle is repeated, the data for early
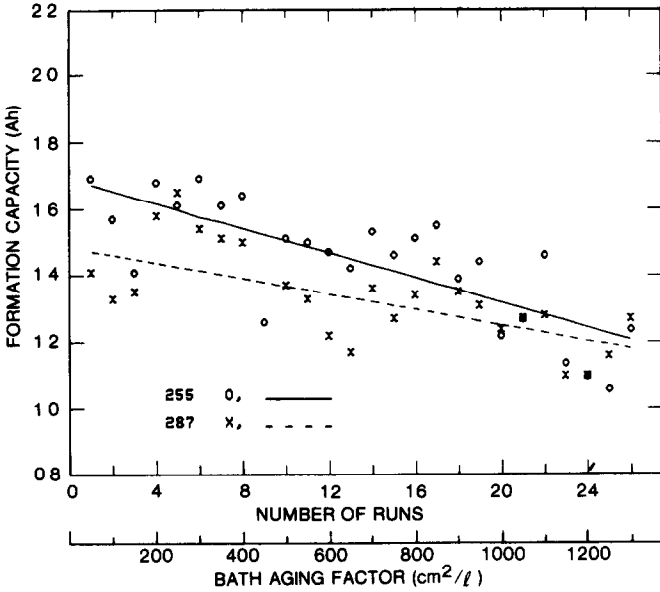
Fig 5 Formation capacity *vs* bath life for 255 and 287 dry powder plaques
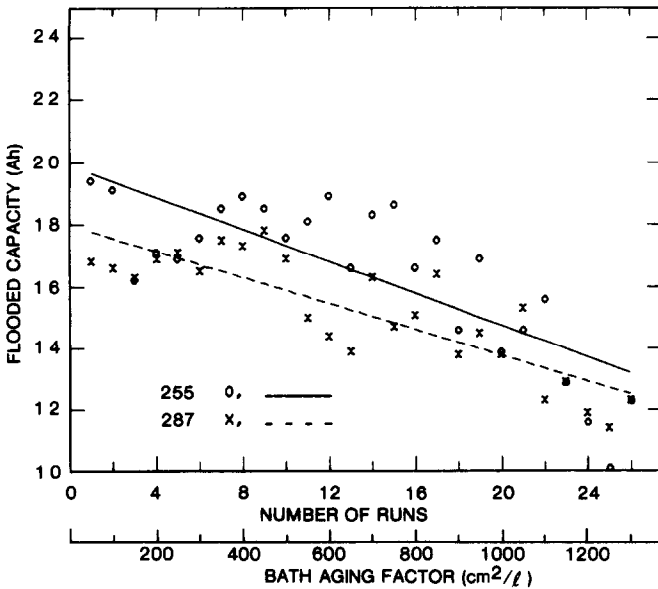

Fig 6 First cycle flooded capacity *vs* bath life for 255 and 287 dry powder plaques

runs again show a capacity increase of about 10%, while the later runs show no improvement.

The cycling of some electrodes was continued, with the results shown in Table 2. In all cases, cycle capacity stabilizes quite early.

TABLE 2

Cycle capacity results

Run no	Type	Cycle capacity (A h)			
		#1	#2	#32	#59
3	255	1 62	1 74	1 78	1 75
3	287	1 63	1 73	1 68	1 69
13	255	1 66	1 72	1 63	1 66
13	287	1 39	1 42	1 39	1 46
24	255	1 16	1 16	1 17	1 22
24	287	1 19	1 19	1 19	1 25

Discussion

The experimental data show a reduction in active material loading with bath usage. One suggested cause for this reduction is a pre-impregnation, time-dependent deterioration of the plaque due to plaque storage in air. Such deterioration is reported to be observable, in some cases, in a matter of weeks after plaque sintering [4]. This effect has been attributed to non-wettability of plaque caused by oxides and carbonates developing in the plaque structure [5]. A second experiment was conducted to test the hypothesis that a reduction in active material loading with bath usage occurs as a result of plaque non-wettability. At the conclusion of the first experiment, and after an additional period of approximately 6 months in this storage environment, plaques were submitted to impregnation at three levels of bath aging. (All materials in both investigations were stored before use in desiccant cabinets under air.) The results of this latter experiment closely approximate those of the former work. Therefore, time-dependent non-wettability does not seem to be responsible for the reduced loading found in this investigation.

Pre-impregnation plaque treatment, such as wet-oxidation [6] to clean and passivate the plaque to preclude corrosion during impregnation, was not performed for the plaque samples of this study. The type of dry powder plaque used in this investigation is inherently clean. Tests for corrosion show the plaque to be passive. This passivity is likely to be due to a passive oxide layer formed at the time of plaque sintering.

Another variable considered in this study was the build-up of sodium in the impregnation electrolyte as the experiment progressed. An effort was made to correlate the sodium concentration with reduced loading. Sodium nitrate was artificially introduced into new impregnation electrolyte at increasing concentration. While some reduction in loading was observed, it was not of sufficient magnitude to explain the bath aging.
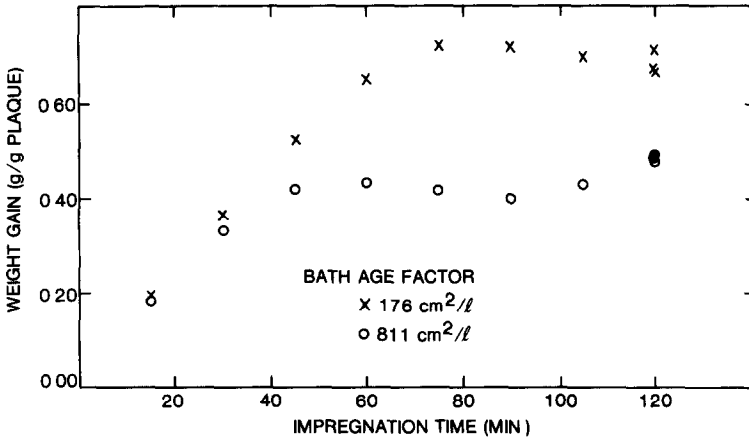
Fig 7 Loading curves for two distinct bath age conditions (255 plaque)

Loading curves were developed for two different bath aging conditions by use of a large bath and by removing plaque samples at intervals during the impregnation. The data plotted in Fig. 7, representing normalized weight gain vs. impregnation time, reveal some information about the nature of the bath aging phenomenon. It can be observed that the initial slope for each loading curve is very nearly the same for the first 30 min of impregnation. These linear portions indicate a process efficiency for $Ni(OH)_2$ deposition of about 38% for both bath conditions. These data are in good agreement with published values [7]. During this initial loading interval, the data suggest that loading progresses normally. However, in the case of the more aged bath it appears that the maximum level of loading (for the process conditions) occurs earlier. Further work is required to define what aspect of the aged bath is responsible for this reduced limitation to active material loading.

Acknowledgments

References

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