A LIGHTWEIGHT NICKEL COMPOSITE ELECTRODE
II. ELECTROCHEMICAL IMPREGNATION

W. LEE

Materials Division, White Oak Laboratory, Naval Surface Weapons Center, Silver Spring, MD 20903-5000 (U.S.A.)

Summary

The structure of sintered nickel composite plaque is characterized by an irregular pore structure with a wide distribution of pore sizes as well as a large median pore dimension compared with sintered-powder nickel plaques. The loading efficiency of the composite plaque was examined as a function of impregnating conditions including current density, temperature, continuity of current flow, the concentration of the impregnating bath and plaque thickness. The study reveals both advantages and disadvantages of the pore structure of the composite plaque with regard to efficient loading of active material. Advantages include reduced impregnation time and complete loading of the active material into thick (over 1.5 mm) as well as thin (less than 1.5 mm) plaques. However, because of fast outward transport of OH^- ions in the composite body which has a large pore size, there is an increased risk of the active material deposition on the plaque surface.

Introduction

In an attempt to reduce the weight and fabrication cost of nickel electrodes for an alkaline cell, nickel composite electrodes which have a sintered body of nickel-coated graphite fibers as the plaque have been developed in our laboratory [1]. The results of charge–discharge cycling tests on these electrodes showed that they can last as long (or in some cases even longer) and achieve storage densities more than 50% higher (over 175 A h/kg) than commercial sintered-power electrodes. However, active material loading of the composite plaques by electrochemical methods did not show consistent loading, and cycling tests on these electrodes generated varied utilizations of the active material.

As shown in the previous report [1], sintered composite plaques have a peak pore diameter of 55 μm, which is about five times larger than that of sintered-powder plaques and have a wide distribution of pore diameters. Besides these structure-related differences, the composite plaques have

lower electrical conductivity than sintered-powder, because they consist largely of graphite fibers. Therefore, the impregnating conditions optimized for powder sinter would not be expected to be the same for the composite plaques.

The efficiency of electrochemical impregnation depends on two types of transport: the generation and outward transport of OH^- ions from the composite plaque to the bulk solution(bath) and the transport of Ni^{2+} ions from the bath to within the porous composite plaque body. Factors determining the production and transport of these ions include pH, temperature, Ni^{2+} ion concentration, current density, mechanical stirring of the impregnating bath and plaque thickness. The aim of this investigation was to find the optimum impregnating conditions which would yield fast and high loading of $Ni(OH)_2$ active material into the nickel composite plaque.

Experimental

Only a brief summary is given here. The detailed information is found in a previous report [1].

Fabrication of sintered nickel composite plaques

Graphite fibers were coated with electroless nickel and sintered, under compression, in dry H_2 atmosphere at 800 °C. Sintered plaques prepared of 0.75, 1.0, 1.5 and 2.5 mm thickness were cut into smaller pieces with dimensions of 2.3 cm × 4.5 cm for impregnation. The porosity of the plaques was 82 - 85%.

Electrochemical impregnation

The method used was basically that reported by Pickett [2] and the nickel salt used was $Ni(NO_3)_2 \cdot 6H_2O$. During impregnation, a constant potential or constant current was used to regulate the cathodic reaction. The potential of the cathode (composite plaque) was controlled not with respect to a reference electrode but with respect to the anode (nickel sheet electrode) using the remote sensing feature of the power supply. This circuitry eliminates the IR drop in the leads at high currents. Concentrations of Ni^{2+} and Co^{2+} (7 wt.% of the Ni concentration) ions in the impregnating bath were monitored with a CARY 16 spectrophotometer.

The pH of the bath (maintained at 85 °C) was regulated by adding dilute HNO_3 when the bath pH reached a pre-selected upper limit. This was accomplished by connecting a pH electrode (Ingold combined electrode with temperature range between 0 and 100 °C) in the bath to a pH controller (Horizon Ecology Model 5997-20) which sent an activation signal to a dispenser when the bath pH reached the pre-selected upper limit [3]. The dispenser, which delivered dilute HNO_3 directly into the bath when activated, consisted of a solenoid valve attached to the tip of a buret containing the acid. The bath pH was controlled to within 0.5 pH units.

For comparison, commercial sintered-powder plaques with the same dimensions and porosity as the composite plaque were also impregnated.

Results and discussion

Mechanical stirring

When the impregnating bath was agitated with a magnetic stirrer to achieve quickly a uniform pH throughout the solution, the loading level of active material was very much reduced regardless of the change in other impregnating conditions (Table 1). As shown in Table 1, the plaques (from #1 - #4) impregnated in the agitated bath have a low loading level of the active material regardless of the bath pH. The plaque (#5) impregnated without agitation has a loading level more than three times higher than that of plaque #3 and more than ca. 14 times higher than that of plaque #2. This result clearly indicates the adverse effect of stirring on loading efficiency. The rapid movement of the bulk solution, as the magnetic bar rotates, disperses OH^- ions accumulated in the close vicinity of the inner surface of the composite plaques and thus hinders the precipitation of $Ni(OH)_2$. The powder sinter (#6) is not affected by stirring because of its much smaller pore size. Based on these results, all further impregnations of the composite plaques were performed without mechanical stirring.

It was found that for composite plaques impregnated in a 1.8 M and 3.5 M Ni^{2+} solution, the optimum pH was 4 and 3, respectively.

TABLE 1

Effect of mechanical stirring on loading of the active material after an impregnation time of 1 hour at a current density of 55 mA/cm^2

Plaque no.	Stirring	Initial weight (g)	pH	Weight gain (g)
1	Yes	1.052	2.0 - 2.5	0.020
2	Yes	1.026	2.5 - 3.0	0.033
3	Yes	1.032	3.0 - 3.5	0.143
4	Yes	1.025	3.5 - 4.0	0.166
5	No	1.025	2.8 - 3.2	0.474
6*	Yes	1.853	2.8 - 3.2	0.509

*Commercial powder sintered plaque.

Current density and nickel concentration

The effect of cathodic current density (mA/cm^2) and Ni^{2+} concentration on the loading level (g/cm^3 of plate volume) is shown in Fig. 1. The loading level is expressed in terms of weight gain of composite plaques after one hour of constant current impregnation. Figure 1 shows that the weight gain curve is much more sensitive to the cathodic current density as the Ni^{2+} concentration increases. For a 1.0 M Ni^{2+} solution the effect of the current

WEIGHT GAIN, g/cm³ OF PLATE VOLUME

1.50

1.25

1.00

0.75

0.50

0.25

3.5M SOLUTION

1.8M SOLUTION

1.0M SOLUTION
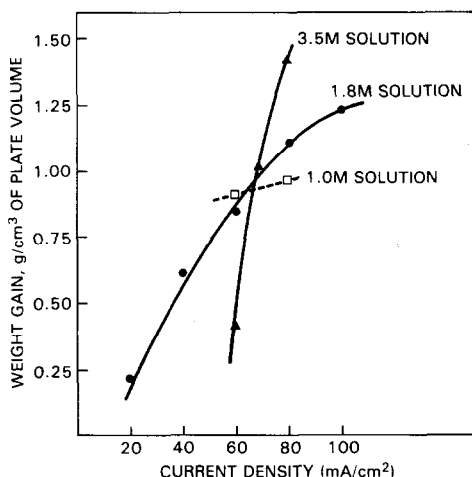
20 40 60 80 100

CURRENT DENSITY (mA/cm²)

Fig. 1. Effect of current density and nickel concentration on the loading level, for a total impregnation time of one hour. The pH of 1.0, 1.8 and 3.5 M Ni^{2+} solutions were 4.5, 4.0 and 3.0, respectively.

density is not profound, whereas for a 3.5 M Ni^{2+} solution the weight gain curve is almost linear in the region between 60 and 80 mA/cm^2. For a 1.8 M Ni^{2+} solution the weight gain curve levels off as the current density exceeds 100 mA/cm^2.

The loading of the active material into the composite plaques of 82% porosity from an impregnating bath containing 1.8 M or 3.5 M Ni^{2+} solution was complete with a weight gain of about 1.6 g/(cm^3 of plate volume). To achieve this loading level it takes about one hour in 3.5 M Ni^{2+} solution and about two hours in 1.8 M Ni^{2+} solution with 80 mA/cm^2 current density in both cases. As the loading level approaches 1.5 g/(cm^3 of plate volume), the plaques start to show some Ni(OH)$_2$ deposits on the plaque surface. This kind of deposition is more severe with impregnations in a 3.5 M Ni^{2+} solution especially when the current density is above 80 mA/cm^2.

The reason why the effect of the current density is not significant in a 1.0 M Ni^{2+} solution bath is possibly because the limiting factor in the loading of the active material is the Ni^{2+} concentration. The sharp increase in the weight gain curve with the increase of the current density for impregnations in a 3.5 M Ni^{2+} solution is attributed to an increase in the production rate of OH$^-$ ions and to an increase in the available Ni^{2+} ions in the precipitation region. The increase in the rate of OH$^-$ ion generation as the current density increases compensates for the lower pH of a 3.5 M Ni^{2+} solution. For a 3.5 M solution, the increase of the current density from 60 to 80 mA (per cm^2 of projected electrode area) increased the loading level by more than a factor of three. At a current density above 60 mA cm^{-2}, the loading level of a 3.5 M Ni^{2+} solution is higher than the loading level of a 1.8 M Ni^{2+} solution.

The optimized current density (in terms of loading level) for the composite electrode in a 1.8 M solution is approximately 80 mA cm^{-2} which is

higher than the value for sintered-powder ($50 \ \text{mA cm}^{-2}$[2]). This difference is greater if the current density is normalized by the real surface area for both plaques. The higher current density required for impregnating the composite plaque is due to its higher electrical resistivity ($\sim 800 \ \mu\Omega$ cm) which is greater than that of sintered-powder ($\sim 200 \ \mu\Omega$ cm).

It has been shown that impregnation in a 3.5 M Ni^{2+} solutions gives faster loading than impregnation in a 1.8 M Ni^{2+} solution, but there is a higher risk of $Ni(OH)_2$ deposition on the plaque surface. Therefore, in subsequent experiments, impregnating conditions that minimized surface deposition were sought while the Ni^{2+} concentration (3.5 M), pH(~ 3) and the bath temperature (85 °C) were held constant.

Constant potential difference impregnation

The accumulation of the surface deposits is detected by monitoring the potential (*versus* anode) of the composite plaque during constant current impregnation. A sudden increase in this potential is indicative of a heavy surface deposition. As a way to minimize this type of deposition, constant potential control was used instead of constant current. The advantage of constant potential control is that the precipitation front, as it moves toward the plaque surface from the inner region of the plaque, slows down as the current density decreases due to loading of the active material. Strictly, control of the cathode potential should be with respect to a reference electrode rather than the anode for constant cathode potential.

The results of constant potential difference impregnation in a 3.5 M Ni^{2+} solution are presented in Table 2. It is seen in Table 2 that a higher initial current density (or higher potential difference) results in a substantially reduced impregnation time for a given loading level of the active material. For example, when the potential difference was increased from -2 to -3 V (approximately), the impregnation time was reduced from 80 to 16 minutes. However, there is an increased danger that $Ni(OH)_2$ will be deposited on the outer surface of the plaques before filling the inside if the potential difference is increased. Measurements of electrode thickness after

TABLE 2

Loading by constant potential difference impregnation

Plaque no.	Applied potential difference (cathode − anode) (V)	Initial current density (mA/cm²)	Impregnation time (minutes)	Weight gain (g/cm³ of plate volume)
36	−2.05	100	80	1.37
35	−2.26	150	44	1.47
42	−2.58	200	30	1.39
45	−3.27	300	16	1.34

pH: 2.5 - 3.0; Ni^{2+} concentration: 3.5 M (+7 wt.% Co); bath temperature: 85 °C.

impregnation indeed showed that heavier outer surface deposition took place with the application of the higher potential difference during impregnation even though the impregnation time was reduced. Since the surface-deposited $Ni(OH)_2$ would not be efficiently utilized during battery cycling, the impregnation potential must be controlled to minimize such deposition.

The onset of heavy surface deposition can be detected by monitoring the current profiles during impregnation (Fig. 2). Figure 2 shows how the cathodic current density changes as the impregnation proceeds. For higher potential differences, the current density has a higher initial value but declines rapidly. Each curve has an inflection point associated with it. It was found by physical examination that deposition of the active material on the surface of the composite plaque is more obvious with time after the inflection. Thus, the impregnation process was stopped shortly after the inflection point was reached to avoid $Ni(OH)_2$ deposition on the plaque surface. The total charge passed before the inflection point decreases as the potential difference increases. This trend together with the weight gain shown in Table 2 seems to indicate that the current efficiency (the amount of loading of active material per unit charge passed) increases as the potential difference increases. However, since the transition from the deposition inside the plaque to surface deposition does not take place as clearly separable sequential steps, it is difficult to determine with accuracy the amount of the deposit inside the plaque. A more rigorous discussion of the efficiency will require more work.

No attempts were made to shorten the impregnation time in a 1.8 M Ni^{2+} solution. Constant potential difference impregnation in this solution
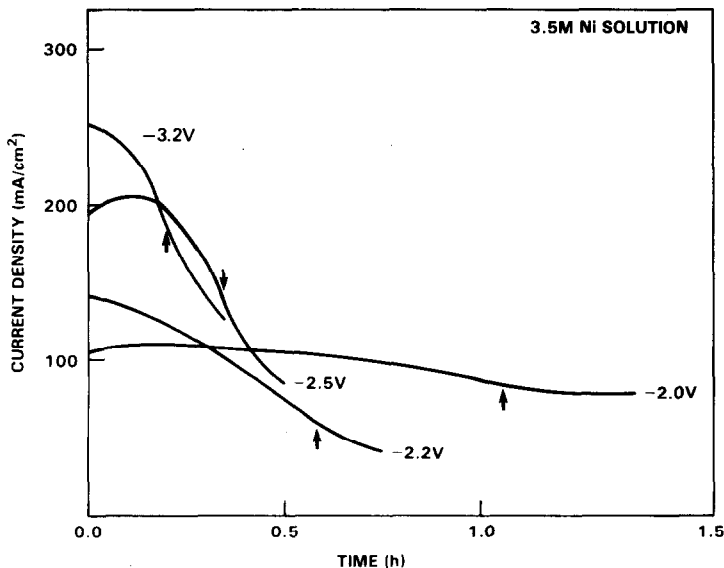

Fig. 2. Current density during constant potential difference impregnation. The applied voltage (cathode − anode) is indicated on each curve. The arrows indicate the inflection points of each curve.

(with 80 mA cm^{-2} initial current density) showed a loading level close to that achieved by constant current impregnation. It is notable that during the constant potential difference impregnation in a 1.8 M Ni^{2+} solution, a current oscillation was observed as shown in Fig. 3. This may be due to periodic adjustments in pH followed by periodic precipitation of Ni(OH)$_2$ active material. Such behavior was not observed in the impregnations carried out in a 3.5 M Ni^{2+} solution.

Intermittent current and temperature effects
        In order to prevent fast movement of the precipitation front during impregnation in a 3.5 M Ni^{2+} solution, two experimental modifications were made to the continuity of current flow and the bath temperature. First, the power supply for impregnation was switched off periodically (Fig. 4). During the power-on period the potential difference was constant while the current decreased as impregnation takes place. During the power-off period the current is zero. This periodic switching-off of the power supply establishes an intermittent current flow. Second, the bath temperature was lowered. These modifications were designed to suppress the production rate of OH$^-$ ions and impede the transport of Ni^{2+} and OH$^-$ ions.
        There were three different modes of current interruptions during constant potential difference impregnation:
        Mode 1 — a period of one minute of power-on followed by one minute of power-off repeated for 60 minutes (for a total of 30 minutes power-on);
        Mode 2 — a period of six minutes of power-on followed by six minutes of power-off repeated for 60 minutes (for a total of 30 minutes power-on);
        Mode 3 — continuous power-on for 30 minutes without interruption.

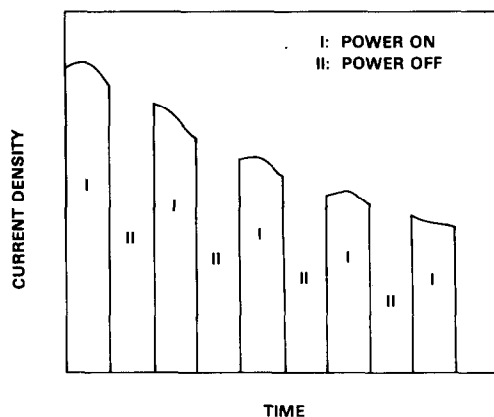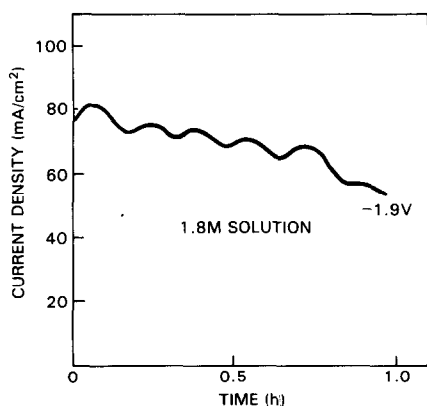The initial current density for these three different modes of impregnation was 80 mA/cm^2.

Fig. 3. Current density oscillations during constant potential difference impregnation for a cathode — anode voltage of −1.9 V.

Fig. 4. Intermittent currents during power interruptions.

The dependence of loading level on bath temperature and the mode of power interruption is shown in Fig. 5. At 25 °C, impregnations with an intermittent current yielded higher loadings than impregnations with the continuous current, whereas the trend was reversed at higher temperatures (over 55 °C). In mode 3 impregnations (continuous current), the lowest loading occurred at 25 °C, while in mode 1 impregnations, the lowest loading took place at 85 °C. Although the highest loading was achieved at 55 °C in mode 3 impregnations, the plaques impregnated at this temperature showed a thick deposit of $Ni(OH)_2$ on the outer surface of plaques. The plaques impregnated at 25 °C did not exhibit any significant deposit on their surfaces.

How the impregnations with the intermittent current at 25 °C increase the loading of the active material is not clear. A possible explanation is that during the power-off period (zero current) Ni^{2+} and NO_3^- ions have time to readjust their concentration profile throughout the porous body so that the rate of OH^- production and the rate of $Ni(OH)_2$ precipitation is increased in the region close to the inner surface of the plaques. A lower rate of production and transport of OH^- ions at 25 °C was deduced from the pH of the impregnating bath. The pH did not rise at all or even dropped during impregnation at this temperature. However, the effect of the anodic electrode process (dissolution of the Ni anode) on the bath pH has to be taken into account for a more rigorous discussion of the change of bath pH.

Increasing the bath temperature results not only in an increase in the rate of inward transport of Ni^{2+} ions from the bulk solution (bath) to the plaque pores, but also, in an even faster rate of outward transport of OH^- ions because of their higher diffusion rate. Therefore during the power-off period, OH^- ions which were produced during the power-on period diffuse out so rapidly that the product of the concentration of Ni^{2+} and OH^- ions does not exceed the solubility product of $Ni(OH)_2$. Therefore, the mode 1 impregnations with the shortest period of power-on and -off resulted in the lowest loadings at 85 °C. Balancing the rate of the outward and the inward transport of OH^- ions and Ni^{2+} ions is very difficult to achieve. The balance
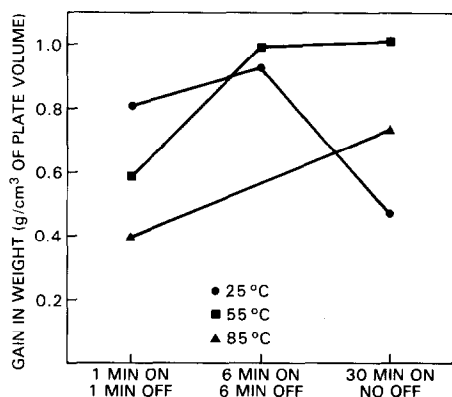

Fig. 5. Effect of current interruptions and bath temperature on loading level (3.5 M Ni^{2+} solution) for a total impregnation time of 30 minutes.

shifts abruptly with only a small change in temperature, Ni^{2+} concentration, current density or pH of the bath.

Plaque thickness

The dependence of the loading level of the active material in the composite plaque on the plaque thickness, for constant current, is presented in Table 3. The impregnation was made in a 1.8 M Ni^{2+} solution. It is seen that the loading level per unit volume of the composite plate does not significantly decrease with the increase of the plaque thickness. The average weight gain is about 1.45 g/(cm^3 of plate volume). It takes about 50% more time to impregnate thick plaques (over 1.5 mm) than thin plaques for similar loading levels. This fact indicates that the transport of Ni^{2+} ions through the composite plaque during impregnation is not hindered by the increase of the thickness. The impregnation of the thinner plaques was stopped after 90 minutes to avoid deposition on the plaque surfaces.

TABLE 3

Dependence of loading level on the composite plaque thickness

Plaque no.	Thickness (mm)	Impregnation time (minutes)	Loading level (g/cm^3 of plate volume)
23	0.74	90	1.52
26	1.02	90	1.44
75	1.52	120	1.33
27	2.54	120	1.40

Nickel concentration: 1.8 M (+7% Co); pH: 4.0; bath temperature: 85 °C; current density: 80 mA/cm^2.

Conclusions

Nickel composite plaques can be impregnated efficiently by the electrochemical method. A current density about 60% higher (80 mA/cm^2) is required to impregnate the composite plaque in a 1.8 M Ni^{2+} solution compared with the current density required for sintered-powder electrodes. By increasing Ni^{2+} concentration to 3.5 M but using the same current density as for 1.8 M Ni^{2+} solution, the impregnation time can be reduced to less than one hour (which is about one half of the time required for the impregnation in a 1.8 M Ni^{2+} solution) to achieve the maximum loading level (1.6 g/cm^3 of plate volume). The impregnation time can be reduced further by increasing the current density, but at the risk of an increased $Ni(OH)_2$ deposit on the outer surfaces of the composite plaques. Such deposition can be suppressed by means of constant potential difference impregnation, lowering the bath temperature or employing intermittent current. Another advantage

of the large open pore structure of the plaques is the ease of impregnating thick plaques (up to 2.5 mm thickness).

References

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