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Impregnation of porous nickel plates by cathodic polarization

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The influence of cathodic polarization during the precipitation of $Ni(OH)_2$ in porous plates prepared from sintered nickel powder has been studied and the influence of the preparation method on the properties of the electrodes examined under conditions which do not lead to the dissolution of the sintered nickel plate. An increase of electrode capacity is recorded for electrodes produced by cyclic polarization between treatment of the plates by immersion in KOH solution.

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1. Introduction

Some remarks are presented in this paper concerning the results described in a former paper [1]. These remarks refer to the efficiency of impregnation of sintered nickel plates by Kandler's method [2], i.e., by cathodic polarization in nickel nitrate solution. The cathodic polarization method is comprehensively described in the literature and covered by many patents. The method is interesting, however, because it allows impregnation of porous plates without corrosion of the sintered nickel plate. The second important advantage of this method is the possibility of impregnating the porous plates in one immersion operation [2, 3].

The aim of this study was to determine the factors controlling the impregnation efficiency of the polarization method described in [1] and to seek conditions which shorten the length of the process whilst obtaining, at the same time, electrodes with the greatest capacity.

2. Experimental

Porous sintered nickel plates (made from type III powder as discussed in the previous paper [1]) were used for the experiments. The plates were immersed in a recrystallized solution of nickel nitrate, density 1.6 g cm^{-3} and pH 2.5. The immersed porous plates were polarized with direct current: the current density was calculated using the geometric surface of the plate. Solid nickel plates were used as anodes. After polarization in nitrate, the immersed plates were put into aqueous KOH solution, density 1.25 g cm^{-3} at 85° C for 15 min. The plates were then taken out of the KOH solution, washed, rinsed and dried at 85° C until they were of constant weight. Electrical tests on the electrodes were performed using the method described in a previous paper [1]. Except for the results given in Table 1 (average from three measurements) all the others are mean values from six measurements.

3. Results and discussion

Measurements of $Ni(OH)_2$ deposition with increasing cathodic current density in nickel nitrate solutions were performed at different temperatures and 30 min electrolysis time. The results are shown in Table 1. The weight gain of plates polarized at 25° C showed a distinct increase for plates polarized with a current density exceeding 60 mA cm^{-2}. When the temperature of solution is higher than 25° C, an increase in plate weight is also observed at lower cathodic current densities. An increase in solution temperature is found therefore to have an advantageous influence on the increase in $Ni(OH)_2$ content in plate pores at a given cathodic current density.

The influence of cathodic current density on electrode capacity was also examined when the polarization process was carried out in a solution at 75° C. The polarization time was chosen in such a way that the same electric charge (0.3 A h cm^{-2}) flowed through each plate, independent of the current value. The results are shown in Fig. 1. Comparing the capacity per gram of $Ni(OH)_2$ as a function of the polarization current density, it is

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Table 1. The influence of temperature and cathodic current density on the gain in weight of plates impregnated by Ni(OH)$_2$ with cathodic polarization

Cathodic current density (mA cm^{-2}) †	*Gain in weight* (g cm^{-3})			
	25° C	50° C	75° C	100° C
0	0.18	0.18	0.24	–
10	0.19	0.36	0.27	0.20
20	0.20	0.55	0.31	–
30	0.24	0.68	0.58	0.74
60	0.58	0.69	0.80	–
90	0.84	0.81	0.97	0.91

† Calculated from the geometric cross-section of the polarized plate.

observed that electrodes polarized with a current density of 15 mA cm^{-2} have the highest capacity. An increase in current density results in a decrease of plate capacity per gram of Ni(OH)$_2$. The capacity of electrodes shows a similar dependence.

The gain in weight of Ni(OH)$_2$ in plate pores is constant over the range studied. However, it must be emphasized that when a low current density is used for polarization, a larger deviation from the average value occurs. The change of electrode capacity is only dependent on the capacity change (per gram of Ni(OH)$_2$) in plate pores as a function of the polarizing current density. The resulting differences can be ascribed to an unequal deposition of hydroxide on pore walls. This can lead to some of the Ni(OH)$_2$ not taking part in the overall process of electrode discharge.

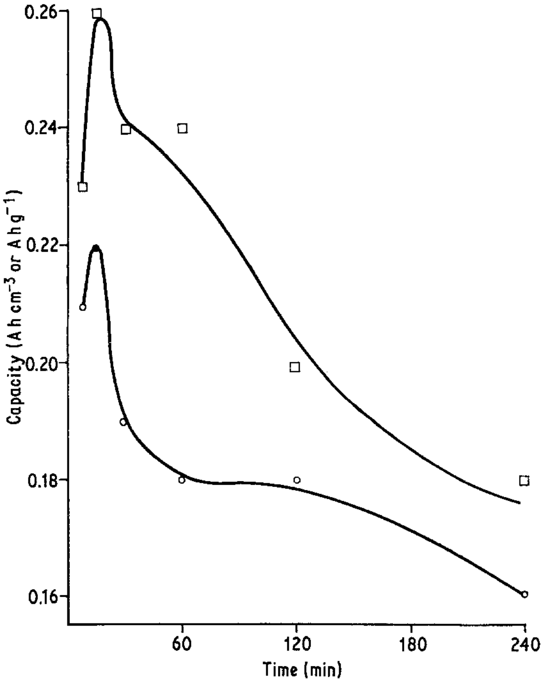

Fig. 1. Electrode capacity (○, A h cm^{-3}; □, A h g^{-1}) as a function of cathodic current density (product $i \times t$ = constant = 0.3 A h cm^{-2}).

In Fig. 2 the influence of cathodic polarization time on the electrode capacity (in A h g^{-1} and A h cm^{-3}) is shown. The porous plates were polarized with cathodic current density of 60 mA cm^{-2}. An extension of the polarization time is also accompanied by a greater deviation from the average gain in weight of Ni(OH)$_2$. This observation is the opposite of that observed using chemical and thermal impregnation methods. In the impregnation method using cathodic polarization, the capacity of the plate in terms of A h g^{-1} Ni(OH)$_2$ is a real value, independent of spurious plate corrosion, and depends only in a limited manner on Ni(OH)$_2$ layer thickness. The capacity of electrodes impregnated by the polarization method is proportional to the polarization time. However, even at the longest polarization time the electrode capacity does not exceed the value of 0.3 A h cm^{-3}.

In the three tests described the precipitation, or rather the plate treatment in KOH solution, is performed after polarization. The properties of electrodes polarized continuously and electrodes polarized for the same time but by a cyclic method were compared in a subsequent test. During the cyclic method the polarization is alternated with precipitation of Ni(OH)$_2$, washing and drying. The polarization was carried out under the conditions given in Section 2. A cathodic current density of 60 mA cm^{-2} was used. The first

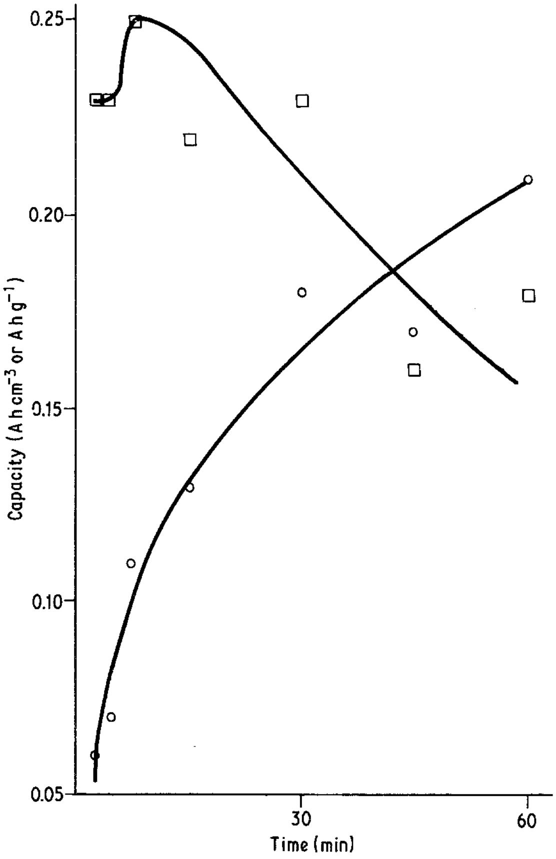

Fig. 2. Electrode capacity (○, A h cm^{-3}; □, A h g^{-1}) as a function of cathodic polarization time.

batch of plates (four impregnation cycles) was polarized for 10 minutes, and the second batch for 40 minutes (one impregnation only). The average results are shown in Table 2.

Comparison of the values obtained for both batches shows that the gain in weight of $Ni(OH)_2$ in plates impregnated for four cycles is much higher then in plates impregnated by the continuous method. The first batch of plates (Table 2) also features a higher capacity per gram of $Ni(OH)_2$. The capacity of electrodes which underwent the interrupted cyclic impregnation reached the value 0.29 ± 0.01 A h cm^{-3}, i.e., at the limit of the value which these electrodes must meet.

The influence of hydrogen-ion concentration on electrode properties, when electrodes were prepared by cathodic polarization (60 mA cm^{-2}, 15 min), was also studied. Between pH values of 0.5 and 3.2, differences in the content of $Ni(OH)_2$ in sinters and electrode capacity were not observed. This similarity is caused by an increase of pH in the solution during polarization. The precipitation of the deposit on the electrode surface is observed when the initial pH of 0.5 changes to 4.2–4.5 close to the electrode after 5–6 minutes. The change of pH and precipitation of the deposit occur more quickly in the pores of sintered electrodes. In consequence, independent of the initial pH value, the increase of $Ni(OH)_2$ weight and the capacity of all electrodes become similar after some minutes of cathodic polarization.

Differences were not observed in the increase of $Ni(OH)_2$ weight and electrode capacity following polarization in solutions of nickel nitrate with concentrations from 1.15 to 1.45 g cm^{-3}. In solutions with concentrations 1.60 g cm^{-3}, a 25% increase in weight gain was found compared with the weight gain in the solution of 1.45 g cm^{-3} concentration.

Table 3 compares the results of impregnating the three types of porous plates (with the properties described previously in [1]) by the interrupted

Table 2. Effect of $Ni(OH)_2$ precipitation by KOH solution on the content of $Ni(OH)_2$ in the sinter and on the electrode capacity

$Ni(OH)_2$ precipitation method	Gain in weight of $Ni(OH)_2$ (g cm^{-3})	Capacity (A h g^{-1} $Ni(OH)_2$)	Capacity (A h cm^{-3})
10 min of polarization followed by $Ni(OH)_2$ precipitation, washing and drying (four impregnation cycles)	1.30 ± 0.02	0.22 ± 0.01	0.29 ± 0.01
40 min polarization followed by $Ni(OH)_2$ precipitation, washing and drying (one impregnation cycle)	0.63 ± 0.02	0.18 ± 0.01	0.12 ± 0.01

Table 3. $Ni(OH)_2$ gain in weight in successive impregnation cycles, and electrode capacity for impregnation, of three types of porous plate

Plate type	*$Ni(OH)_2$ gain in weight in successive impregnation cycles* (g cm^{-3})						*Capacity*	
	1	2	3	4	5	*Total*	(A h g^{-1} $Ni(OH)_2$)	(A h cm^{-3})
I	0.35	0.40	0.30	0.16	0.07	1.28	0.24 ± 0.01	0.31 ± 0.01
II	0.39	0.38	0.30	0.17	0.07	1.31	0.26 ± 0.01	0.34 ± 0.01
III	0.34	0.36	0.25	0.20	0.11	1.25	0.24 ± 0.01	0.30 ± 0.01

polarization method. The impregnation conditions have been the same as in the former test (polarization time, 10 min). The gain in weight of $Ni(OH)_2$ in succeeding impregnation cycles is similar for the three types of porous plates. Slightly better results are obtained for the type II porous plate. For this kind of plate the highest capacity per gram of $Ni(OH)_2$ (0.35 A h cm^{-3}) has been obtained. The capacity of electrodes obtained from the remaining two types of plate also exceeded 0.3 A h cm^{-3}.

Obviously the whole of the results described relates to the precipitation of β-$Ni(OH)_2$ in the pores of the sinter; this then oxidizes during charging to nickel oxyhydroxide according to the reaction:

$$\beta\text{-Ni(OH)}_2 \rightleftharpoons \beta\text{-NiOOH}.$$

During cathodic polarization the hydroxide precipitated in the sinter pores must be composed of the modification α-$3Ni(OH)_2 \cdot 2H_2O$. According to Bode and other authors [4] this modification changes into β-$Ni(OH)_2$ by treatment with KOH solution, as in this work.

4. Conclusions

A green deposit of nickel hydroxynitrate precipitates in plate pores during the cathodic polarization of porous plates in nickel nitrate solution. The simple dependence of the $Ni(OH)_2$ precipitation rate on temperature points to the important part played by the diffusion of Ni^{2+} ions in the immersion process in conjunction with polarization. During polarization, some hydrogen bubbles evolve on the walls of the pores, especially on those nearer to the external surface of the plates, which probably hinder Ni^{2+} ions diffusing to the inside of the plates. Therefore, in most studies, attempts are made to choose conditions for cathodic polarization which avoid hydrogen evolution or limit it significantly (i.e., low current densities and low temperature are used).

However, the adoption of such conditions leads to an excessive polarization time of several hours. On the basis of the results obtained it can be stated that when a low current density is used for polarization, not only the process duration is extended, but also the capacity of the electrodes is very variable. Furthermore it seems to be difficult to obtain a high capacity of $Ni(OH)_2$ (0.26 A h g^{-1}) when the polarization is a slow process, especially at low temperatures.

Some importance must be attached to the way $Ni(OH)_2$ crystallizes in porous plates. A good crystallization of $Ni(OH)_2$ in porous plates seems to be the principal factor determining $Ni(OH)_2$ loading efficiency in the polarization method. The increase of solution temperature facilitates the diffusion of Ni^{2+} ions deep into the plates and assists in the formation of more crystalline $Ni(OH)_2$.

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