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THE THERMAL STABILITY OF THE β-Ni(OH)$_2$–β-NiOOH SYSTEM

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ABSTRACT

The thermal decomposition reaction of the β-Ni(OH)$_2$–β-NiOOH system prepared by electrochemical oxidation of β-Ni(OH)$_2$ was investigated by TG, DTG and static thermal analysis. Results obtained at various oxidation states and the effect of temperature on the decomposition reaction are presented. It was concluded that two types of dehydration reaction are operative and the oxidation of NiO is also a possible process during the thermal dehydration of partly charged (electrochemically oxidized) nickel hydroxide.

INTRODUCTION

The chemistry of the positive active material of the alkaline Ni–Cd accumulators has engrossed the attention of researchers for almost a century. In spite of the large amount of work dealing with the Ni(OH)$_2$–NiOOH system there are some unsolved problems which require further study. The thermal behaviour of the β-Ni(OH)$_2$–β-NiOOH system prepared by controlled electrochemical oxidation of β-Ni(OH)$_2$ has hardly been investigated [1–3]. Fortunately, a fair amount of information is available about the thermal stability of pure nickel hydroxide.

The complete dehydration of β-Ni(OH)$_2$ takes place above 200 °C according to the reaction

$$\mathrm{Ni(OH)_2 \rightarrow NiO + H_2O} \tag{1}$$

as has been reported in numerous papers [4–9]. However, the decomposition reaction of nickel oxyhydroxide has not been discussed in detail. The thermal stability of γ-NiOOH has been studied by Aia [10] who showed that the dehydration of charged material (which was accompanied by the evolution of O_2 and H_2O) occurred at a lower temperature than in the uncharged state. Rademacher et al. [1] came to the same conclusion in the case of β-NiOOH. The main difficulty in the thermal characterization of nickel oxyhydroxides is that the oxidation product of nickel hydroxide is a heterogeneous mixture and not a well-defined compound. Detailed analysis of

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partly charged nickel hydroxide has revealed that the β-Ni(OH)$_2$–β-NiOOH system is a mixture of two solid solutions, namely a phase of oxidation state 2.25 and a phase of oxidation state 2.75 [11,12]. Consequently, the actual composition of the charged state cannot be given simply by the usual stoichiometry.

The aim of this paper is to investigate the decomposition reaction of partly charged nickel hydroxide at various states of charge and at various temperatures. Results obtained by conventional thermal analysis (TG, DTG) may contribute to a better understanding of the β-Ni(OH)$_2$–β-NiOOH system and will provide a good opportunity for comparing the thermoanalytical properties of partly charged nickel hydroxide with that of pure nickel hydroxide reported in the literature.

EXPERIMENTAL

Nickel hydroxide powder was prepared from nickel sulphate (Reanal, analytical grade) and potassium hydroxide (Reanal, analytical grade) using deionized water (specific conductivity $\gamma \approx 200\ \mu$ Sm^{-1}) under the conditions described below. β-Ni(OH)$_2$ was precipitated from 1 mol dm^{-3} nickel sulphate solution by 11 mol dm^{-3} potassium hydroxide solution at room temperature. The precipitate was filtered and washed until no sulphate ion was detected by barium chloride solution. The precipitated nickel hydroxide was dried at 100 °C and ground to a powder ($<$ 0.1 mm). In order to decrease the sulphate content of the dried material (2–3 wt%) the nickel hydroxide was treated in 0.1 mol dm^{-3} potassium hydroxide solution at 90 °C and was then washed and dried again. This procedure gave a β-phase product (ASTM, 14-117) confirmed by X-ray diffraction measurement. The dried nickel hydroxide contained less than 0.5 wt% of sulphate impurity.

Samples of β-Ni(OH)$_2$ were ground with 20 parts by weight of graphite flake. The mixture (8.3 g) was then compressed in a 4.5 cm diameter disc at 10 MPa. Each of the discs was enclosed in a nickel-plated perforated steel pocket in which two nickel meshes were placed to prevent the active material from falling out. The electrodes were placed in individual plastic cells containing nickel plate counter electrodes and the cells were filled with a solution of 4.5 mol dm^{-3} potassium hydroxide. In order to prepare partly charged nickel hydroxides the electrodes were subjected to the following charge–discharge cycles: (1) charge at $C/10$ rate for 15 h, discharge at $C/10$ rate to H_2 evolution (where C is the theoretical capacity); (2)–(4) charge at $C/10$ rate for 15 h, discharge at $C/5$ rate to H_2 evolution. When the desired state of oxidation was attained in the fourth discharge, the discharging process was interrupted and the electrode material was washed free of alkali and dried in a desiccator over phosphorus pentoxide in vacuum.

The nickel and graphite contents of the dried nickel oxyhydroxide were analyzed by conventional EDTA titration and by gravimetric analysis respectively, after the samples had been dissolved in sulphuric acid solution. Iodometric titration was used for the determination of the change in oxidation state during the thermal decomposition reaction.

Two types of thermoanalytical measurements were carried out in air using a Mettler thermoanalyzer calibrated with K_2SO_4 and $KClO_4$ standard substances: (1) TG and DTG curves were recorded at a heating rate of 6 °C min^{-1} and at a sample weight of 40–50 mg (the heating was terminated at 500 °C); (2) thermogravimetric curves were recorded at constant temperature.

RESULTS AND DISCUSSION

Since all of the samples contained a relatively large amount of graphite (~ 20 wt%) the weight loss curves of graphite-free β-$Ni(OH)_2$ and β-$Ni(OH)_2$ mixed with graphite were recorded. Comparing the two TG curves presented in Fig. 1, it can be seen that the presence of graphite has no effect on the dehydration reaction. In both cases the minimum of the DTG curve could be observed at 297 ± 3 °C and this result is in good agreement with the data reported in the literature [4–8]. The thermogravimetric curve of partly charged nickel hydroxide is shown in Fig. 2. In this case the minimum of the DTG curve appeared at 247 ± 3 °C showing that the thermal dehydration of partly charged nickel hydroxide takes place at a lower temperature than in the uncharged state. The lower thermal stability of partly charged nickel hydroxide is also indicated by the fact that the charged material begins to

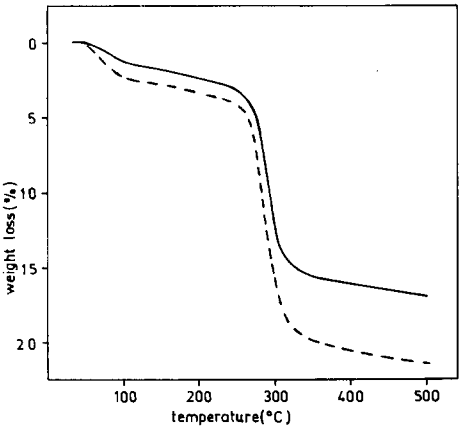

Fig. 1. Thermogravimetric curves for pure β-$Ni(OH)_2$ (- - - - - -) and for β-$Ni(OH)_2$ mixed with graphite (———).

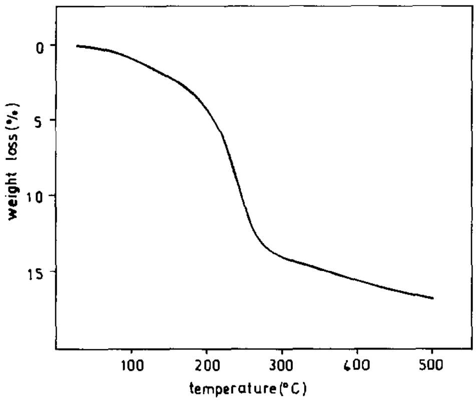

Fig. 2. Thermogravimetric curve of the β-Ni(OH)$_2$–β-NiOOH system at oxidation state 2.52.

decompose at about 100°C, whereas the decomposition of β-Ni(OH)$_2$ occurs above 200°C (see Figs. 1 and 3). Owing to the low stability of the partly charged material, the removal of adsorbed water, the elimination of intercalated water and the decomposition reaction take place almost simultaneously. Therefore, the lack of intercalated water in the β-NiOOH-type compounds, concluded from X-ray measurements [13], cannot be directly confirmed. However, the relatively low value of the overall water content (3–5 wt%) estimated from the measured composition of the β-Ni(OH)$_2$–β-NiOOH system (see Table 1) may be an indication of the absence of intercalated water. Results obtained by TG, DTG and chemical analyses are summarized in Table 1. Although the TG and DTG curves of the partly charged nickel hydroxide were measured at various states of charge (oxidation state 2.3 to 2.8) no differences were observed in these curves indicating that the dehydration temperature is independent of the oxidation state. However, we shall see later that the degree of decomposition depends on the oxidation state, (Fig. 3).

TABLE 1

Characteristics of samples studied by TG and DTG

Sample	Graphite content (wt%)	Oxidation state	Total weight loss from 50 to 500°C (wt%)	DTG peak (°C)	Ni content (wt%)
Ni(OH)$_2$	–	2.00	21.4	297±3	60.0±0.5
Ni(OH)$_2$ + graphite	19.3±0.3	2.00	17.0	297±3	48.4±0.5
Ni(OH)$_2$–NiOOH	19.4±0.3	2.37±0.02	16.9	247±3	47.8±0.5
Ni(OH)$_2$–NiOOH	19.1±0.3	2.52±0.02	16.8	247±3	47.8±0.5
Ni(OH)$_2$–NiOOH	19.2±0.3	2.80±0.02	17.0	245±3	48.2±0.5

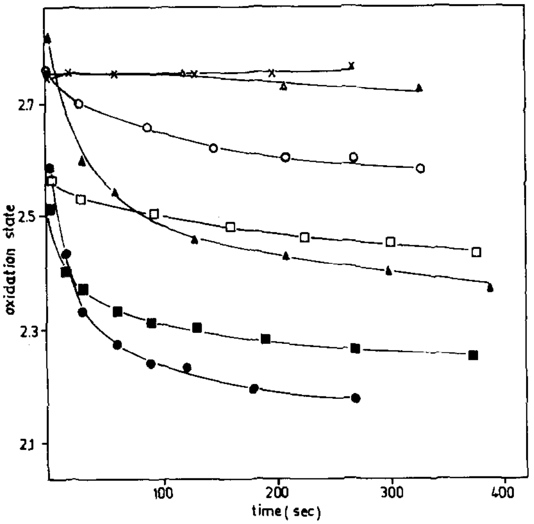

Fig. 3. Isothermal decomposition curves of partly charged nickel hydroxide at various temperatures: (×) 50 °C; (△) 100 °C; (○), (□) 150 °C; (■), (▲) 180 °C; (●) 200 °C.

In order to give a more complete picture of the dehydration process of nickel oxyhydroxide we measured the change in oxidation state of partly charged nickel hydroxide at various temperatures and at various states of charge. The temperature was changed from 50 to 200 °C and the oxidation state was within the range 2.5–2.8. It is not surprising, as can be seen in Fig. 3, that the initial rate of reaction increases with increasing temperature. However, the initial fast reaction period is followed by a decrease in the reaction rate. Following a period of some hours the rate of the decomposition reaction tends to an almost constant low value although the dehydration process is far from complete. This low value of reaction rate is almost independent of the temperature (see Fig. 3). Without a formulation of the dehydration process it is not easy to explain this thermal behaviour. It has already been mentioned that partly charged nickel hydroxide is a heterogeneous mixture of two solid solutions. Therefore, to the first approximation, two types of decomposition reaction can be expected. The first type is the dehydration of nickel oxyhydroxide

$$NiOOH \rightarrow NiO + 0.5H_2O + 0.25O_2 \qquad (2)$$

and the second is the dehydration of nickel hydroxide (see reaction (1)).

We measured the weight loss of partly charged nickel hydroxide at various temperatures. If we suppose that the weight loss observed below 150 °C mainly originates from the loss of adsorbed water, the relative amount of the β-Ni(OH)$_2$–β-NiOOH system transformed in reactions (1) and (2) can be determined. From this and from the observed change in oxidation state at a given temperature the relative amounts of NiO formed

TABLE 2

Effect of temperature on the dehydration process

Temperature (°C)	Oxidation state	Relative amount of $Ni(OH)_2$-NiOOH transformed in 270 min (wt%)	Relative amount of NiO formed in the dehydration of NiOOH (wt%)
150	2.57	13±2	90±10
180	2.52	29±2	90±10
180	2.80	37±2	100±10
200	2.58	49±2	85±10

in reactions (1) and (2) can be calculated. These results are listed in Table 2. It is noticeable that reaction (2) is the predominant process during the decomposition of the β-$Ni(OH)_2$–β-NiOOH system below 200 °C. Consequently, reactions (1) and (2) do not take place in entirely the same temperature range as may be concluded from the DTG measurements (only one peak can be observed on the DTG curves). In the case of the β-$Ni(OH)_2$–β-NiOOH system the decrease in NiOOH content starts at about 100 °C and it is continuously operative during the dehydration process; significant decomposition of $Ni(OH)_2$ occurs above 200 °C.

In the foregoing discussion we have considered the possible dehydration processes in order to furnish a basis for the explanation of the significant decrease in the decomposition rate observed during heat treatment (Fig. 3). This explanation lies in the fact that reaction (2) is the predominant process below 200 °C. If we assume that in addition to the dehydration of NiOOH the oxidation of NiO also takes place at a considerable rate, then we can interpret the low rate of the dehydration process. It can be considered as the consequence of a thermodynamically controlled reversible process (reaction (2)) which is not far from an equilibrium state. Here, we must mention that the formation of Ni^{3+} ions during the thermal decomposition of $Ni(OH)_2$ has already been verified by several researchers [8,9,14,15]. Their results have shown that not only does the dehydration of $Ni(OH)_2$ take place, but an oxidation process should also be expected. In accordance with this latter statement, the oxidation of NiO prepared in argon has been observed directly by Fievet et al. [15] when a sample of NiO was exposed to the air. These results reported in the literature provide additional proof of the plausibility of the interpretation outlined above.

CONCLUSIONS

Thermal analysis of the β-$Ni(OH)_2$–β-NiOOH system has revealed that this partly charged material begins to decompose at 100 °C, whereas the decomposition of pure β-$Ni(OH)_2$ occurs above 200 ° C. In the case of partly charged nickel hydroxide two types of decomposition processes can be expected, namely the dehydration of $Ni(OH)_2$ and the dehydration of NiOOH. These two reactions do not take place entirely simultaneously. Below 200 ° C the decrease in the NiOOH content is the predominant process. The observed change in oxidation state of the charged material at a given temperature suggests that in addition to the dehydration of NiOOH and $Ni(OH)_2$ the oxidation of NiO to NiOOH is also a possible reaction, which causes a premature decrease in the rate of the decomposition process.

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