

THERMOANALYTICAL INVESTIGATION OF THE Ni(OH)₂-NaOH SYSTEM

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ABSTRACT

Investigating an Ni(OH)₂+NaOH mixture with a thermoanalytical method we have stated that at 190°C an endothermic DTA peak referring to a so-far unknown process appears together with a weight loss.

Carrying out measurements in argon or air atmospheres, the phenomenon is observed in the same way. It is probable that, in the case of pure Ni(OH)₂, the Ni(OH)₂=NiO+H₂O dehydration reaction occurring at 280°C takes place at lower temperatures under the influence of NaOH built-in between the planes of the Ni(OH)₂ crystal.

INTRODUCTION

Ni(OH)₂ is the main component of the positive active material most often used in alkaline accumulators, and its thermoanalytical properties have already been investigated by many authors. Some research workers studied the connection between the thermoanalytical and electrochemical properties of Ni(OH)₂, others studied the dehydration process of Ni(OH)₂.

Aia [1] tested a well-crystallized Ni(OH)₂ sample in a hydrothermal apparatus, in the temperature range 200-400°C and in the pressure range 0.2-2.1 kbar. He stated that the dehydration process



takes place at $285 \pm 5^\circ\text{C}$ independently of pressure. However, he could not detect the hydrothermal rehydration of NiO either in water or in KOH at 40%. Interlayer water is found in addition to water adsorbed in Ni(OH)₂. This is characteristic of so-called α -modifications. According to Dennstedt [2] the water content favourably influences the electrochemical oxidizability of Ni(OH)₂ and it was proved by thermoanalytical investigations that most of the interlayer water was removed together with water arising from dehydration at the same temperature. He attributed this to the interlayer water being hydrogen-bonded to the OH groups in Ni(OH)₂.

Rodemacher [3] treated $\text{Ni}(\text{OH})_2$ at 200°C hydrothermally for 13 h. Under the influence of this treatment the electrochemical activity fell to about one-sixth. The crystallite size increased from 21.0 to 41.5 nm on the (001) crystal plane. The temperature of the endothermic DTA peak belonging to the decomposition (eqn. 1) rose from 240 to 341°C .

Greaves et al. [4] tested $\text{Ni}(\text{OH})_2$ samples made in a different way, applied to the positive electrode of alkaline accumulators thermoanalytically. The samples contained 0–5.2% added Co agent and their crystallite size was 4–17 nm on the (001) grid plane. The DTA peak belonging to reaction (1) appeared at 279 – 325°C depending on the Co content and the crystallite size.

The $\text{Ni}(\text{OH})_2$ –NaOH system has not yet been tested thermoanalytically. This could promote a better understanding of the processes connected with the operation of alkaline accumulators as well as the production of positive active material. During the charging of alkaline accumulators KOH molecules are built into the $\text{Ni}(\text{OH})_2$ electrode from the electrolyte. During discharge these are removed and water molecules take their place [5]. On the other hand the positive active material is mostly produced in such a way that $\text{Ni}(\text{OH})_2$ is separated by alkali from the nickel salt, then after filtration the very alkaline precipitate is desiccated [6]. During this process the mutual effect of the $\text{Ni}(\text{OH})_2$ –NaOH system can arise due to the considerably higher temperature compared to the accumulators.

EXPERIMENTAL AND RESULTS

The tests were carried out with a Q 1500-D Derivatograph (MOM, Budapest) which is suitable for recording TG, DTG and DTA functions simultaneously. The heating rate was 5°C min^{-1} , and the end temperature was 400°C .

The tests were carried out with basic materials of different types, the compositions of which can be seen in Table 1. This was necessary to decide whether the thermoanalytical behaviour of the $\text{Ni}(\text{OH})_2$ –NaOH system is influenced by graphite or cobalt which is often applied to the positive active material of alkaline accumulators.

TABLE 1

The basic materials tested

Type	Composition (%)		
	$\text{Ni}(\text{OH})_2$	Graphite	$\text{Co}(\text{OH})_2$
1	75 ± 2	18 ± 2	3 ± 1
2	93 ± 2	–	3 ± 1
3	78 ± 2	18 ± 2	–

The basic materials were made by a process applied in the production of positive active material of alkaline accumulators, so that $\text{Ni}(\text{OH})_2$ to be found in them can be considered in its main mass as poorly crystallized $\beta\text{-Ni}(\text{OH})_2$; the crystallite size is 4 nm on the (001) grid plane.

To the basic materials NaOH, pulverized to powder fineness in a knife-grinder, was mixed in different quantities and these samples were tested in Ar and air. Besides NaOH the interaction of $\text{Ni}(\text{OH})_2$ and some other salts and alkalis (KOH , $\text{Ba}(\text{OH})_2$, LiOH , Na_2SO_4 , Na_2CO_3) was also tested.

KOH is used as the electrolyte of the alkaline accumulators. $\text{Ba}(\text{OH})_2$ and LiOH are known additive agents to alkaline accumulators. Na_2CO_3 and Na_2SO_4 became involved with $\text{Ni}(\text{OH})_2$ during production of the positive active material. Interaction was experienced only in the case of NaOH and KOH used in amounts larger than 5%.

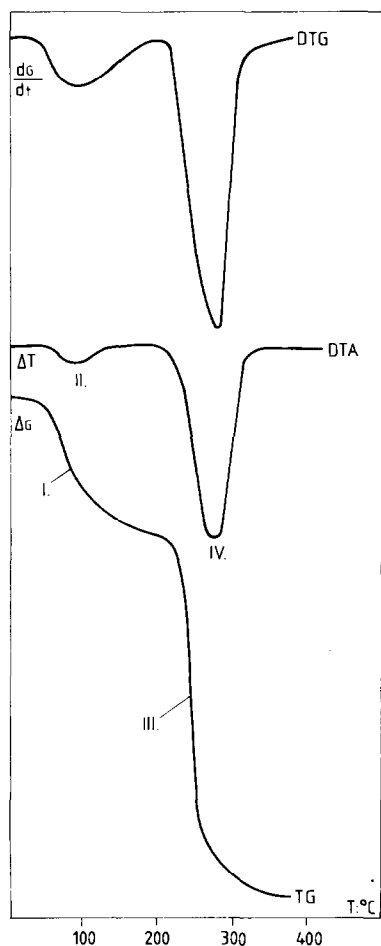


Fig. 1. Type A thermoanalytical curves. Characteristic of pure $\text{Ni}(\text{OH})_2$ and such compounds in which there is no mutual effect between $\text{Ni}(\text{OH})_2$ and the added material.

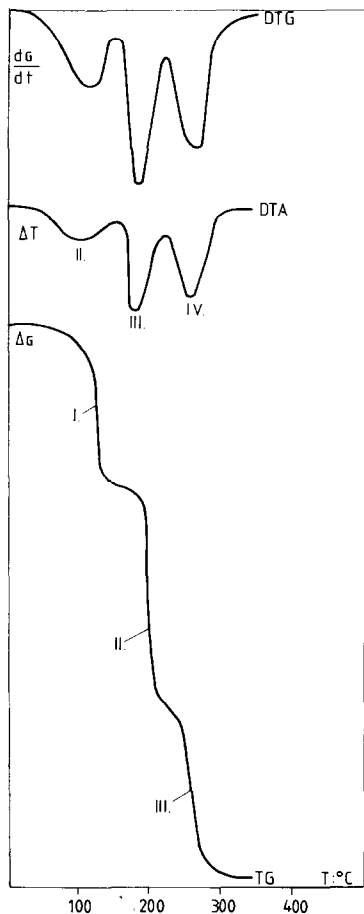


Fig. 2. Type B thermoanalytical curves. Characteristic of samples containing a small amount of alkali (10–15%).

During the tests we obtained four types of thermoanalytical curves (A, B, C and D), which are shown in Figs. 1–4. On the DTA curves four endothermic peaks can be found (I–IV) for which the following explanation can be given:

DTA I. Appears at $\sim 60^{\circ}\text{C}$ in the case of samples containing a high NaOH content (25–80%). There is no change in weight. It can also be observed in the case of pure NaOH (Fig. 4).

DTA II. Appears at $80\text{--}140^{\circ}\text{C}$ with a weight loss (TG I) indicating the removal of adsorbed water (Figs. 1–4).

DTA III. Appears at $170\text{--}210^{\circ}\text{C}$ together with a weight loss (TG II) in the case of samples containing NaOH or KOH. DTA III indicates the mutual effect of $\text{Ni}(\text{OH})_2\text{--NaOH}$ and $\text{Ni}(\text{OH})_2\text{--KOH}$ which has not been shown thermoanalytically up to now. Our test set us a target to state how the ratio

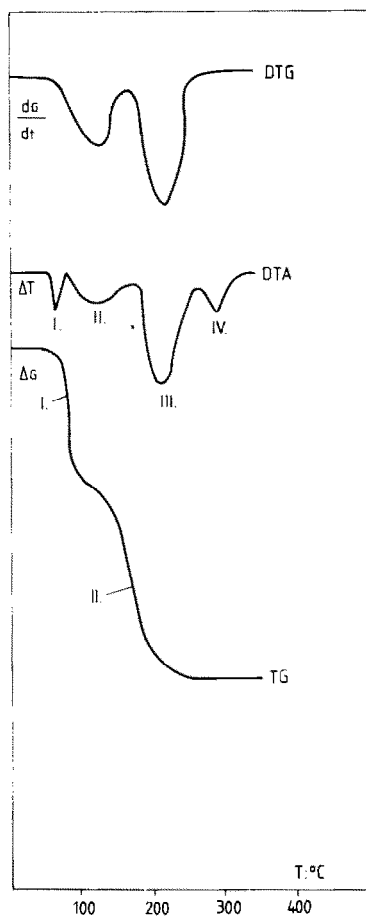


Fig. 3. Type C thermoanalytical curves. Characteristic of samples containing a moderate amount of alkali (15–25%).

$\text{Ni}(\text{OH})_2\text{-NaOH}$ and the applied atmosphere influence this mutual effect (Figs. 2–4).

DTA IV. At 250–290°C there is also a weight loss for samples containing a small amount of alkali (0–25%) (TG III) (Figs. 1–2). In this case, process (1) is probably indicated. In the case of samples containing much alkali (25–80%), there is no weight loss. In this case, the melting of NaOH is suggested (Fig. 4).

Thermoanalytical curves of type A were obtained (Fig. 1) for the basic material marked with 1, 2 and 3 as well as for compounds in which the interaction of the mixed material and $\text{Ni}(\text{OH})_2$ could not be perceived. Such materials were: $\text{Ba}(\text{OH})_2$, LiOH, Na_2CO_3 , Na_2SO_4 and up to 5% NaOH and KOH. On the DTA curves corresponding to these thermoanalytical curves, endothermic peaks of type II and IV are found.

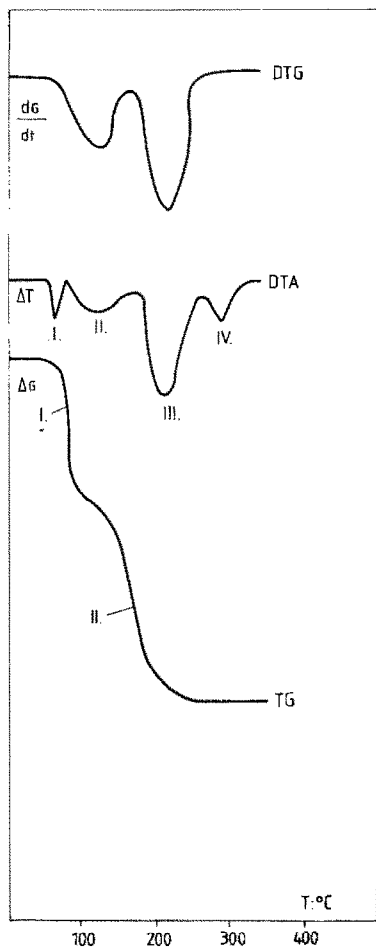


Fig. 4. Type D thermoanalytical curves. Characteristic of samples containing a large amount of alkali (25–80%).

Thermoanalytical curves of type B (Fig. 2) are characteristic of samples containing a small amount of alkali. For these samples, endothermic DTA peaks of type II, III and IV appear.

For type C (Fig. 3), the endothermic peaks II and III appear on the DTA curves. This is characteristic of samples containing 15–25% alkali.

Thermoanalytical curves of type D (Fig. 4) can be observed from samples of high alkali content (25–80%). In this case endothermic peaks of type I, II, III and IV also appears on the DTA curve.

TABLE 2
Significant derivatographic data

Description of the sample		Atmos- phere	DTA III		DTA IV		ΔG % whole	Type of thermo- analytical curve
Basic material type	Additive		ΔG (%)	DTA (°C)	ΔG (%)	DTA (°C)		
1		air	–	–	86.3	280	86.3	A
2		air	–	–	95.6	275	95.6	A
3		air	–	–	90.2	278	90.2	A
1	5% NaOH	air	–	–	81.7	280	81.7	A
1	5% KOH	air	–	–	81.2	285	81.2	A
1	5% Ba(OH) ₂	air	–	–	82.1	280	82.1	A
1	5% LiOH	air	–	–	85.1	285	85.1	A
1	5% Na ₂ CO ₃	air	–	–	83.9	290	83.9	A
1	5% Na ₂ SO ₄	air	–	–	82.8	295	82.8	A
1	10% Ba(OH) ₂	air	–	–	85.5	270	85.5	A
1	10% LiOH	air	–	–	85.5	280	88.5	A
1	10% Na ₂ CO ₃	air	–	–	81.9	285	81.9	A
1	10% Na ₂ SO ₄	air	–	–	80.5	290	80.5	A
1	10% KOH	air	68.0	175	28.0	260	96.0	B
3	20% NaOH	air	88.9	210	–	–	88.9	C
2	10% NaOH	air	68.2	190	22.4	255	90.6	B
2	10% NaOH	Ar	58.3	182	44.7	260	103.0	B
2	20% NaOH	air	83.9	188	–	–	83.9	C
2	20% NaOH	Ar	87.5	192	–	–	87.5	C
2	40% NaOH	air	88.5	195	–	274	88.5	D
2	40% NaOH	Ar	107.1	195	–	275	107.1	D
2	80% NaOH	air	93.2	210	–	285	93.2	D
2	80% NaOH	Ar	94.6	216	–	288	94.6	D

On the TG curves three stages can be observed. TG I is connected with the removal of adsorbed water, and appears in the case of all samples tested. TG II and III can be perceived, depending on the composition of the sample, together with DTA III and IV.

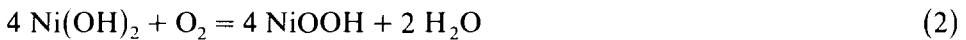
In order to illustrate the observed weight loss we assumed, when evaluating the TG curves, that the processes indicated by DTA III and IV were both a consequence of dehydration process (1). Therefore the measured weight loss, taking into consideration the Ni content and mass of the tested sample, was presented with the theoretical value to be expected on the basis of the decomposition (1), marked ΔG (%). We emphasize that the above-mentioned generalization of process (1) serves only for introducing the results numerically. Our measurement results are shown in Table 2.

EVALUATION AND CONCLUSIONS

Among the $\text{Ni(OH)}_2 + \text{Ba(OH)}_2$, $+ \text{LiOH}$, $+ \text{Na}_2\text{CO}_3$ and $+ \text{Na}_2\text{SO}_4$ systems no mutual effect appeared at the applied tested parameters. On application of 10% or more of NaOH or KOH a new endothermic DTA peak (DTA III) appeared at $190 \pm 20^\circ\text{C}$ together with a weight loss which refers to the interaction between the above-mentioned materials and Ni(OH)_2 . The interaction is independent of the cobalt and graphite contents of the Ni(OH)_2 sample tested.

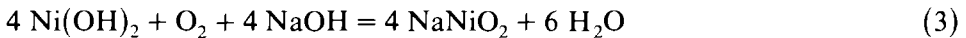
At 10–15% NaOH (or KOH) the Ni(OH)_2 decomposed in two steps (DTA III and IV). Increasing the quantity of NaOH, the decomposition removed entirely to the direction of the process indicated by DTA III. The whole weight loss (TG II + TG III), which corresponds to about 1 mol $\text{H}_2\text{O}/1$ mol Ni(OH)_2 , and the temperature connected with DTA III barely depended on the NaOH content.

Between the weight losses (ΔG) of the tests carried out in Ar and in air atmospheres a variable difference was observed, in argon the weight loss was, however, somewhat greater in every case than in air. This may be caused by the following oxidation reaction or one similar to it:



The weight loss of reaction (1) is 19.4%, that of the reaction (2) is 12.5%, due solely to O_2 absorption.

The reaction



can be supposed; this is, however, accompanied by a higher weight loss (26.8%) than process (1).

Summarizing it can be stated that NaOH interacts with Ni(OH)_2 at 190°C in both argon and air. The investigations referred to the Ni(OH)_2 –NaOH system, but from some measurements which were carried out using KOH the conclusion can be drawn that there is a similar mutual effect between Ni(OH)_2 and KOH.

The interaction process can be combined with oxidation processes in the presence of O_2 ; it is probable, however, that in the presence and absence of O_2 dehydration process (1) takes places at lower temperatures under the influence of NaOH. This supposition is confirmed, since between the crystal plates of Ni(OH)_2 , as it is already known, alkali hydroxide molecules can be built in. It is probable that the built-in alkali hydroxide molecules facilitate the dehydration process. For judging the removal processes more closely, further investigations referring to the structure and composition of the material were carried out besides the thermoanalytical investigations.

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