

Experimental device for investigations of the formation process of the Ni(OH)₂/NiOOH electrode. Part II*

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Abstract

A new method for investigating the formation of Ni(OH)₂ to NiOOH is presented. It is based on observations of the black formation-moving-zone. Additionally a circuit diagram for the different electronic and ionic currents due to the experiment is introduced. Some results obtained on different nickel hydroxides are given.

Introduction

The Ni(OH)₂/NiOOH couple is used as the positive electrode for rechargeable (sealed) Ni/Cd accumulators. The capacity of the cell is very sensitive to the electrochemical properties of the positive electrode. The nickel hydroxide acting as the active material is produced by chemical precipitation of nickel salts (NiSO₄, Ni(NO₃)₂) with alkaline solutions (KOH, NaOH). Due to the low intrinsic electronic conductivity of Ni(OH)₂ it is necessary to incorporate the active material into an electronically conducting matrix which can be, for example, a nickelized perforated steel plate or a nickel foam substrate.

To obtain an electrochemical active behaviour of the positive electrode it is necessary to have an initialization process, the so-called formation. This formation of the nickel hydroxide is done during the first charge and discharge cycles of the battery and, therefore, seems to be a relatively easy procedure. Despite the fact that this process is done thousands of times every day very little is known about the complex elementary processes which determine the formation.

The formation can be described as a process which provides an effective chargeability and dischargeability of the electrode by forming a special composition and spatial distribution of the electrochemical active material in the bulk of the electrode.

Experimental

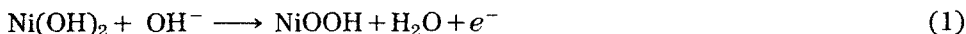
The change in colour of the nickel hydroxide electrode during the oxidation (formation) process from Ni(OH)₂ (green) to NiOOH (black), offers

*Part I is ref. 1.

the possibility of studying the formation process via optical investigations. To use that effect the device shown in Fig. 1 was developed.

The compressed nickel hydroxide sample, which was made by squeezing off the suspension attained by the previous precipitation process [2], is kept between two porous nickel electrodes of the DSK type [3] in a tube made out of plexiglas. When applying electrical current to this arrangement the following processes will occur:

oxidation of the $\text{Ni}(\text{OH})_2$ at the anode according to eqn. (1):



hydrogen evolution at the cathode:



During the formation process the formation front, which is visible from the colour change of the sample from green to black, moves from the anode to the cathode leaving the oxidized NiOOH behind. When the formation is completed oxygen evolution at the anode will start.



Therefore, it is possible to calculate the amount of charge which was necessary for the formation process via the difference of the amounts of charge for the hydrogen and oxygen evolution. In order to do this it is necessary to measure the quantity of hydrogen and oxygen being evolved during the formation. With the help of Faraday's laws the amount of current can be calculated from the data of the gas volumes. One millilitre of hydrogen under standard conditions (20 °C, 0.1013 Mpa) corresponds to a charge of 2.39 mA h; one millilitre of oxygen amounts to twice as much.

In our device it was necessary to have a good electrical contact of the sample and to achieve controlled evolution and drainage of the reaction gases in order to avoid problems by gas bubbles or an arising overpressure. Therefore, the sample was contacted by three-layer DSK electrodes. At the inner layer (working layer), which is made out of a coarse skeleton of Raney-nickel, the evolution of the gases should proceed. The outer layers (cover layers) of nickel (anode; higher overvoltage for oxygen evolution than Raney-nickel) and copper (cathode; higher overvoltage for hydrogen evolution than Raney-nickel) guarantee a controlled evolution of the gases at the working

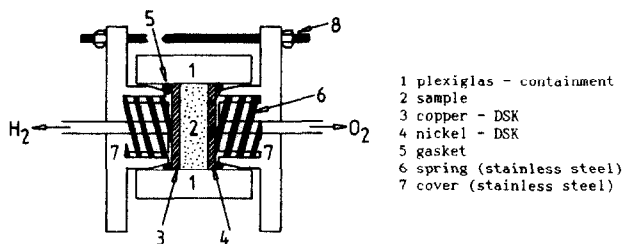


Fig. 1. Plexiglas-holder for the sample.

layer; their fine pore system with high capillary pressures prevent the gases from passing the layer in the direction of the sample. To provide an exit for the gases to the 'backside' of the electrodes, a part of the corresponding cover layers was removed.

Figure 2 shows the measurement device with all peripheral equipment. The evolved gases are registered by two bubble counters recording the rising gas bubbles via an optoelectrical device. A photocamera recording the moving of the formation front is released at constant periods by the computer. Due to the change in the ohmic resistance during the formation of the poorly conducting $\text{Ni}(\text{OH})_2$ to the well conducting black NiOOH it was necessary to measure the ohmic resistance. This was realized by an a.c. milliohmmeter working at 1 kHz using four-terminal configuration.

All data of the experiment were recorded by a computer.

Circuit diagram of the different flows during the formation

The phenomenon during the formation of the nickel hydroxide in the measurement device described above can be illustrated and easily understood with the help of the circuit diagram shown in Fig. 3. The constant d.c. current applied to the sample has three different possibilities of passing between the cathode and the anode.

In the very first moment the sample consists of the divalent green nickel hydroxide, which is well known to be a bad conductor. Therefore the current will pass the sample as an ionic current developing hydrogen at the cathode and oxygen at the anode. With the beginning of oxidation of $\text{Ni}(\text{OH})_2$ to NiOOH the oxygen evolution will stop and after some time the black formation front will appear at the anode moving in the direction of the cathode. Due to the good conductivity of the generated black NiOOH the current can cross the zone of formation as a pure electronic current. At the front of the

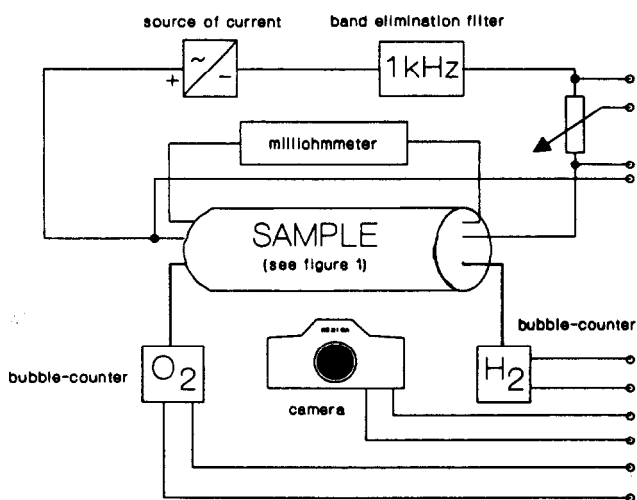


Fig. 2. Measurement device.

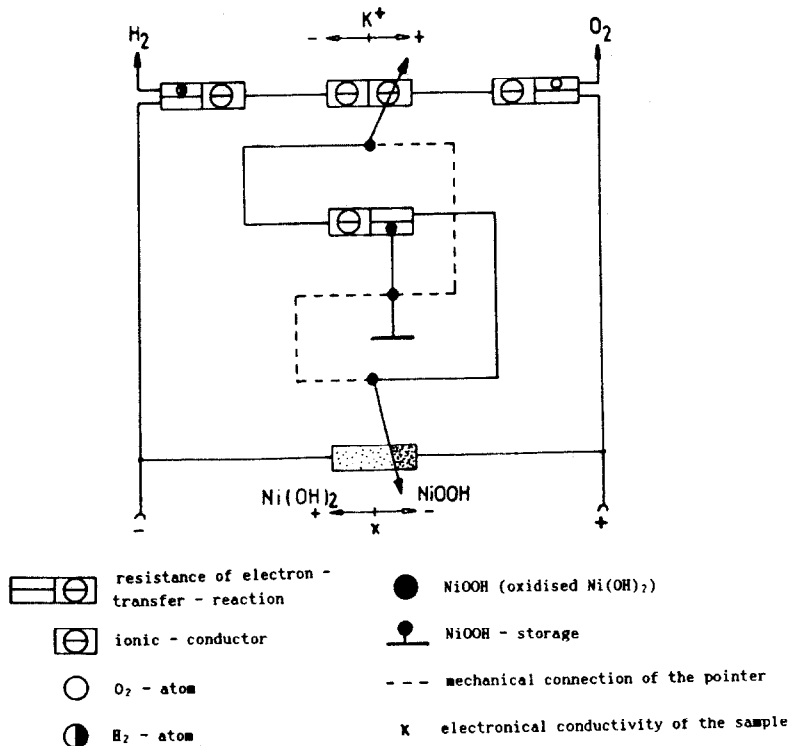
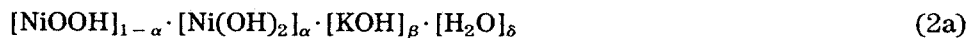


Fig. 3. Schematic circuit diagram of the flows during formation.

formation an electronic to ionic charge transfer reaction occurs together with an additional formation of $Ni(OH)_2$. At the cathode hydrogen is evolved via a second charge transfer reaction from the electrolyte to the copper DSK electrode. If the electrolyte has a high concentration, electrolysis can happen in addition to the formation of $Ni(OH)_2$ leading to a further oxygen evolution. As soon as the front of the formation reaches the cathode, an electrical short circuit is generated interrupting all electrochemical reactions.

Results

Equation (2) does not describe the real composition of the active material. This composition might be better described by the formula (2a), which takes into account the fact that during oxidation of $Ni(OH)_2$ alkali ions (e.g. K^+) were intercalated into the lattice.



In order to get details about the influence of this intercalation process and other doping effects on the formation behaviour of the nickel hydroxide a number of tests were carried out varying the following parameters:

- grain size of the nickel hydroxide
- type of alkali ion in the electrolyte (K^+ , Li^+)
- electrolyte concentration
- doping of the nickel hydroxide (Fe, Co, Al)

As described above, the optical progress of the black formation front is recorded by a photocamera. The values obtained by this method are compared with the theoretical values, which were calculated in the following manner.

The amount of charge $I_F \times dt$ necessary for the formation within the increment of time dt corresponds to the progress of the black formation front $qc \, dx$:

$$dx = (I_F \, dt) / (qc) \quad (4)$$

I_F can be calculated from the difference between the developed amount of hydrogen and oxygen:

$$I_F = \left(\frac{dV_{H_2}}{dt} \times 2.39 \frac{\text{mA h}}{\text{ml}} \right) - \left(\frac{dV_{O_2}}{dt} \times 4.79 \frac{\text{mA h}}{\text{ml}} \right) \quad (5)$$

The typical profile of the movement of the formation front (optical and theoretical) and the change in the a.c. resistance during the experiment is shown for a lithium/potassium-doped sample in Fig. 4.

It can be seen from Fig. 4 that the optical formation precedes the theoretical formation in the region from 0 to 80%. This effect was more or less observed for all samples examined and led to incompletely oxidized parts; these could be noted when breaking the sample after removing the plexiglas-holder.

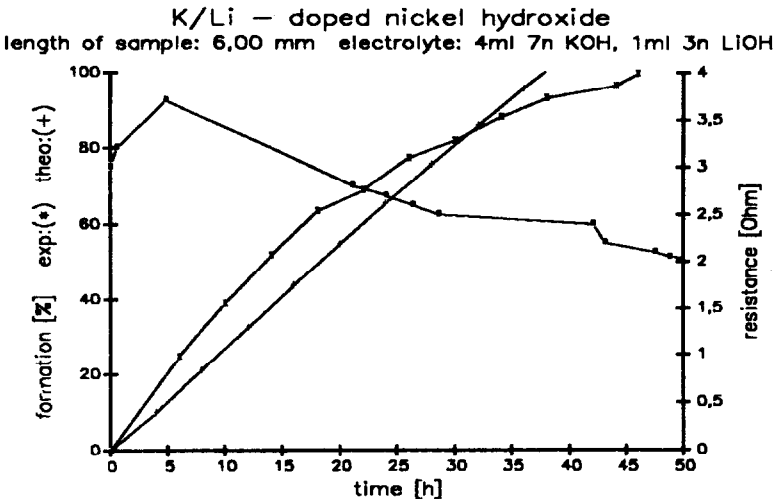


Fig. 4. Temporal change of the formation front (optical and theoretical) and time dependent decrease of the a.c. resistance.

The grain size did not have a remarkable influence on the formation behaviour of the nickel hydroxide sample [4].

The specific a.c. resistance measured at the end of the formation of all examined nickel hydroxide samples was found to be in the region of about 10 to 100 Ω cm which is 1 to 2 orders of magnitude lower than stated for NiOOH in the literature.

By varying the concentration of KOH from 0.5 to 12 N it was found that the best results were achieved by using a concentration of 6 ± 1 N, where the conductivity of the solution has its maximum. An increase of the concentration combined with an increase of oxygen evolution (electrolysis). Decreasing the concentration down to very small values (less than 1 N) resulted in the quantity of material formed being only 80%.

The doping with lithium led to an increased formation of the examined samples. This was independent of the amount of lithium added to the electrolyte (see Fig. 5). Additionally, the capacity of the active material increased remarkably [5], which corresponds to the results obtained by Dennstedt [6]. As this observation correlates with satisfying values for the activation energy for the self-discharge [5], doping with lithium seems to be recommendable.

Doping of the nickel hydroxide with cobalt did not support the formation; in spite of often being used in commercial cells as a doping material of the positive electrode the cobalt doped samples showed decreased electrochemical values (low capacity and low activation energy for the self-deactivation process [5]).

The values for the doping of the active material with aluminium (10 and 20 mol.%) proved to be totally different. While the 10% doping showed the typical current-voltage characteristic as was observed with the potassium and lithium impregnated samples, the (constant) current of 50 mA broke down after 35 h of formation (the voltage reached its highest peak of

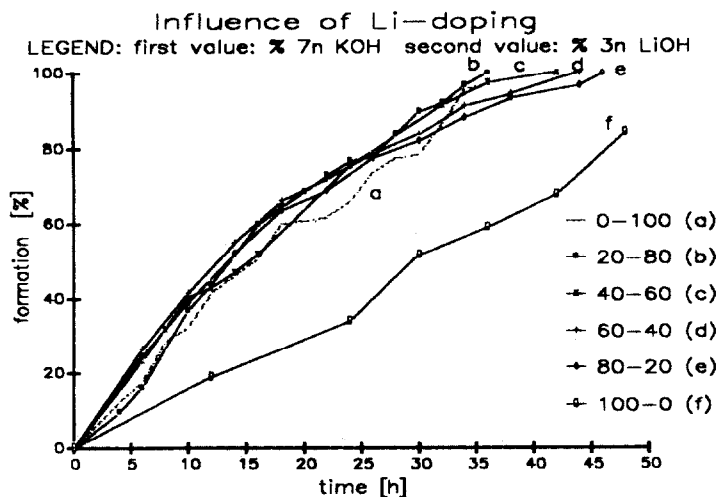


Fig. 5. Influence of lithium doping on the formation behaviour.

30 V limited by the controller used) using a doping of 20 mol.%. Therefore the formation was interrupted at approximately 60%. The only possible explanation for this result is a passivation of the electrochemical active nickel hydroxide by a layer of aluminum oxide. This effect is confirmed by the poor capacity of the electrode, while the 10% doping yields good results [5].

The samples which were doped with iron (so-called 'siderophilic' nickel hydroxide [7]) showed again a totally different behaviour on formation. There was no movement of a grouped 'formation front' observed; the oxidation led to the growth of 'needles' of NiOOH. The explanation for this phenomenon is based on the assumption that well conducting magnetite Fe_3O_4 , which can be formed at the potential of the NiOOH formation, increases the conductivity of the oxidized material. Thus, a growth of dendrites is supported. This theory was confirmed by an experiment using graphite as additional conducting material. The result was a decreased formation of needles. The reason is that the current is now able to reach most of the unformed nickel hydroxide particles via the additional path. Despite this unusual behaviour the samples doped with iron produced good results with respect to self-discharge and capacity. In addition to its immunity against poisoning with iron [7], this material could be a promising basis for the reactivation of the Ni/Fe accumulator with a decreased rate of corrosion and therefore could be one alternative to the Ni/Cd accumulator.

List of Symbols

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|------------------|---|
| I_F | the part of the total current, which forced the formation (mA) |
| c | volume capacity of $\text{Ni}(\text{OH})_2$ (mA h cm^{-3}) |
| dx | progress of formation (cm) |
| dt | increment of time (h) |
| q | cross section of the sample (3.46 cm^2) |
| V_{H_2} | volume of the developed hydrogen (ml) |
| V_{O_2} | volume of the developed oxygen (ml) |

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