

## Stability enhancement of the CoOOH conductive network of nickel hydroxide electrodes

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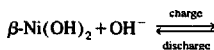
### Abstract

Nickel hydroxide is used as the electrochemically active material in positive electrodes of rechargeable alkaline batteries. Well-spread CoOOH is used as the conductive network to enhance the utilization of the nickel hydroxide. If the nickel hydroxide electrode is subjected to a negative potential it may display an enduring capacity loss due to an irreversible electrochemical reduction of CoOOH. In this paper it has been demonstrated that the addition of MnO<sub>2</sub> to nickel hydroxide pressed powder electrodes ensures 100% capacity retention after imposing reducing conditions.

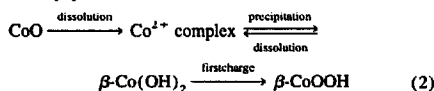
**Keywords:** Nickel hydroxide electrode; Nickel–metal hydride batteries; Cobalt oxyhydroxide; Manganese oxide; Electrodes

### 1. Introduction

Nickel hydroxide, Ni(OH)<sub>2</sub>, [1] is used as the electrochemically active material in positive electrodes of rechargeable alkaline nickel–cadmium [2] and nickel–metal hydride batteries [3]



The practical capacity of the positive nickel hydroxide electrode depends on the efficiency of the conductive network connecting the nickel hydroxide particles with the current collector. The conductive network may be divided into a coarse and a fine part. In the case of so-called pressed powder electrodes (also called mass electrodes) [4] the coarse part usually consists of nickel powder. The fine part is established by  $\beta\text{-CoOOH}$  which is an electrical conducting Co<sup>3+</sup> compound that is electrochemically formed from CoO (Co<sup>2+</sup>) during the first charge in an alkaline medium such as 7 M KOH [5]



By deposition via the solution,  $\beta\text{-CoOOH}$  is well spread at the surface of the nickel hydroxide particles and ensures a very efficient conductive network leading to a higher utilization of the nickel hydroxide. By means of  $\beta\text{-CoOOH}$  the gravimetric capacity of nickel hydroxide increases typically from 200 to 250 mAh g<sup>-1</sup>. These values refer to pressed powder electrodes (buttons) and a discharge current of about 50 mA g<sup>-1</sup>.  $\beta\text{-CoOOH}$  is considered to be a stable compound that cannot be reduced during usual discharge cycles [5].

However, if the electrochemical potential at the nickel hydroxide electrode decreases far below its usual working potential of about +350 mV versus Hg/HgO, the conductive network  $\beta\text{-CoOOH}$  may be electrochemically reduced to poor soluble  $\beta\text{-Co(OH)}_2$  or even to Co, resulting in a deteriorated fine part of the network. The reduction of  $\beta\text{-CoOOH}$  commences thermodynamically below a potential of +90 mV versus Hg/HgO [6]. Probably the coarse part of the conductive network (nickel powder) of pressed powder electrodes is not sufficient fine to include all reduced regions in its electrical pathways. In this case the recovery of sufficient amounts of  $\beta\text{-CoOOH}$  during the charge of subsequent cycles is not possible and the positive electrode shows an irreversible capacity loss due to a diminished utilization. In contrast to that, the nickel sinter electrode [7] never displays such a capacity loss because its conductive network, a nickel sinter body, is intrinsically stable against reduction.

Using laboratory-scale rechargeable alkaline nickel–metal hydride button cells we demonstrate that the addition of

MnO<sub>2</sub> to a positive pressed powder electrode is able to ensure 100% capacity retention after subjecting the positive electrode to negative potentials. The latter is achieved by using cells whose negative electrode possesses a higher capacity than that of the positive electrode. If such cells are externally loaded in its discharged state, a negative potential is imposed at the nickel hydroxide electrode. In this case the negative excess capacity may be discharged by the reduction of  $\beta$ -CoOOH at the positive electrode.

## 2. Experimental

The results presented in this paper are from several laboratory-scale rechargeable nickel–metal hydride button cells [8,9]. Apart from the composition of the mixture for the positive electrode these cells were produced and treated under the same conditions. The most important items were the following.

The active material of the negative electrodes consisted of a commercial available hydrogen storage alloy. The materials to prepare the mixture for the positive electrode were commercial available Ni, Co, CoO, MnO<sub>2</sub> and Ni(OH)<sub>2</sub>. The positive as well as negative electrodes were prepared by pressing the corresponding mixtures into pellets (buttons) which were covered with a nickel mesh. Before cell assembling the positive electrodes were treated overnight in 7 M KOH at 80 °C. This process ensures an excellent distribution of the Co<sup>2+</sup> complex. The approximate dimensions of the button cells were 25 mm in diameter and 6 mm in height involving a commercial available separator and 250  $\mu$ l electrolyte (7 M KOH) per cell. The excess capacity of the negative electrode was created by means of the usually irreversible oxidation of CoO and Co to  $\beta$ -CoOOH at the positive electrode during the first charge of the cell. The cells were charged and discharged at room temperature with a current of 50 mA and the cutoff cell voltage was chosen to be 1000 or 700 mV. At the beginning six cycles were performed. Afterwards the cells were electrically loaded with an external resistor having a resistance of 2  $\Omega$  and stored for three days at 65 °C (the high temperature was used to enhance the kinetics of the reduction process). After imposing reducing conditions at the positive electrode in this way, the cells were cycled five times to determine their remaining capacities.

## 3. Results

Fig. 1(a) shows the cell capacity as function of the cycle number of representative laboratory-scale standard-type nickel–metal hydride button cells (indicated by the denotation 0%) discharged to a cutoff voltage of 1000 mV. The positive electrode composition of these cells is 60% Ni(OH)<sub>2</sub>, 9% CoO, 1% Co and 30% Ni. After imposing reducing conditions at the positive electrode (cycle number 7) the standard-type cells (denoted as 0%) display a capacity loss of

about 20%. Using a cutoff voltage of 700 mV the capacity loss is even higher, about 30%, as pointed out in Fig. 2 where the representative behaviour of a further series of cells is exhibited. This result seems to be reasonable because the low cutoff voltage 700 mV (compared with 1000 mV) may already initiate the reduction of  $\beta$ -CoOOH. After completing the sixth cycle these cells probably contain somewhat reduced and deteriorated  $\beta$ -CoOOH and therefore the subsequent more severe reducing conditions lead to a higher total loss of  $\beta$ -CoOOH compared with those cells that were cycled with a cutoff voltage of 1000 mV.

Successful attempts to overcome this capacity loss were achieved by adding manganese oxides to the positive electrode. Manganese oxides, especially MnO<sub>2</sub>, are known to have a high oxidation potential. Therefore the presence of MnO<sub>2</sub> in the positive electrode seemed to be an promising candidate to diminish the reduction of  $\beta$ -CoOOH and/or to support its recovery by electrochemical oxidation. Fig. 1(a) shows, in comparison with the standard-type composition (0%), the results of three representative cells containing MnO<sub>2</sub> in the positive electrode, i.e. in this case 60% Ni(OH)<sub>2</sub>, 9% CoO, 1% Co, 27% Ni and 3% MnO<sub>2</sub>. Obviously the presence of merely 3% MnO<sub>2</sub> is able to ensure 100% capacity retention. Also in the case of the more severe treatment using a cutoff voltage of 700 mV, 3% MnO<sub>2</sub> does completely avoid an enduring capacity loss as pointed out in Fig. 2.

The discharge characteristics of cells with 0 and 3% MnO<sub>2</sub> before imposing reducing conditions at the positive electrode do not reveal significant differences as shown in Fig. 1(b). Fig. 1(c) shows an earlier decrease in cell voltage for the MnO<sub>2</sub>-free cells and simply reflects the capacity loss due to the reduction. In contrast to the discharge behaviour, the charge curves reveal more remarkable differences between 0 and 3% MnO<sub>2</sub> (see Fig. 1(d)–1(g)). At cycle number 1, the first cycle at after assembling the cells, the step-like behaviour at the beginning (Fig. 1(d)) may be assigned to the oxidation Co<sup>0</sup> (Co) and Co<sup>2+</sup> (CoO)  $\rightarrow$  Co<sup>3+</sup> ( $\beta$ -CoOOH). As clearly revealed in Fig. 1(d) this step is less pronounced for cells with 3% MnO<sub>2</sub> indicating the presence of less Co<sup>2+</sup> and Co<sup>0</sup> compared to MnO<sub>2</sub>-free cells. This is probably due to the pretreatment of the electrodes before cell assembling (see Experimental) at which MnO<sub>2</sub> may oxidize parts of CoO and Co (see also discussion below and Fig. 3). The molar ratio CoO/MnO<sub>2</sub> at the positive electrode mixture should distinctly be greater than 1. Otherwise, it may be possible that the electrode pretreatment converts a great part of CoO and Co into  $\beta$ -CoOOH impeding a reliable establishment of the excess capacity at the negative electrode.

Fig. 1(e) displays the charge curve during the sixth cycle. Apart from the first cycle at which  $\beta$ -CoOOH is formed, this behaviour is representative for all cycles before imposing reducing conditions (cycle numbers 2–6 in Fig. 1(a)) and merely reflects the charge of the nickel hydroxide.

The charge curve during the first cycle after imposing the reducing conditions (cycle number 7 in Fig. 1(a)) is exhibited in Fig. 1(f). At the beginning the cells with 3% MnO<sub>2</sub>

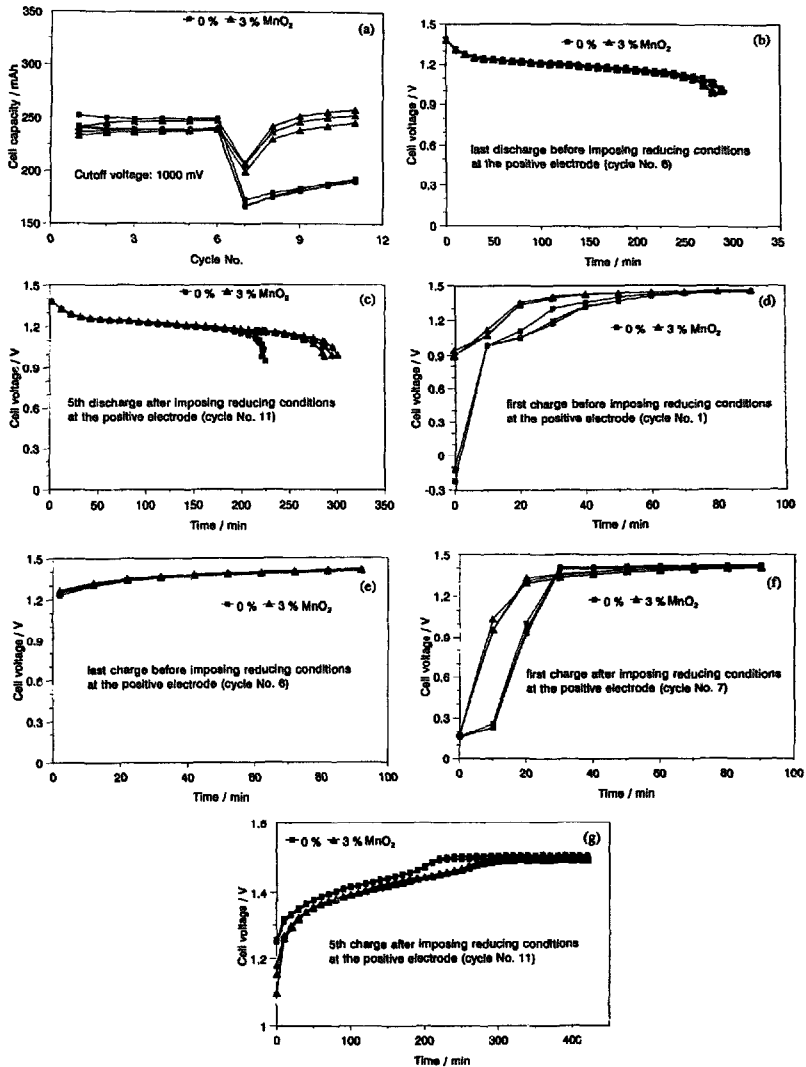


Fig. 1. (a) Cell capacity vs. cycle number of nickel-metal hydride laboratory-scale button cells differing merely in the composition of the positive electrode. Between the 6th and 7th cycle the discharged cells were loaded with  $2 \Omega$  and stored for three days at  $65^\circ\text{C}$ . (b) Representative discharge curves before imposing reducing conditions at the positive electrode. (c) Representative discharge curves after imposing reducing conditions at the positive electrode. (d) Beginning part of the charge curves of the first cycle (cycle number 1 in Fig. 1(a)). (e) Beginning part of the charge curves of the last cycle before imposing reducing conditions at the positive electrode (cycle number 6 in Fig. 1(a)). (f) Beginning part of the charge curves of the first cycle after imposing reducing conditions at the positive electrode (cycle number 7 in Fig. 1(a)). (g) Charge curves of the fifth cycle after imposing reducing conditions at the positive electrode (cycle number 11 in Fig. 1(a)).

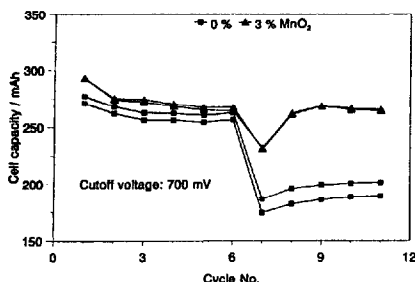


Fig. 2. Cell capacity vs. cycle number of nickel-metal hydride laboratory-scale button cells differing merely in the composition of the positive electrode. Between the sixth and seventh cycle the discharged cells were loaded with  $2 \Omega$  and stored for three days at  $65^\circ\text{C}$ .

display a nearly continuous increase in voltage whereas the  $\text{MnO}_2$ -free cells show a step-like behaviour. The latter observation at the  $\text{MnO}_2$ -free cells suggests that greater amounts of  $\text{Co}^{2+}$  are oxidized to  $\text{Co}^{3+}$  and therefore it is reasonable to conclude that more  $\beta\text{-CoOOH}$  was reduced compared with those cells containing 3%  $\text{MnO}_2$ . In accordance to that, after completing the increase in voltage the cells with 3%  $\text{MnO}_2$  display a lower voltage than those without  $\text{MnO}_2$  (see Fig. 1(f)). That reflects its better chargeability of the nickel hydroxide due to a less deteriorated conductive network in agreement with its higher capacity (see cycle number 7 in Fig. 1(a)).

The charge curve of the fifth cycle (Fig. 1(g)) reveals the enduring distinct behaviour between the cells with 0% and 3%  $\text{MnO}_2$  and is representative for the behaviour after imposing reducing conditions at the positive electrode (see cycle number 7-11 in Fig. 1(a)). The  $\text{MnO}_2$ -free cells early reach a voltage plateau pointing out the attainment of the fully charged state. Those with 3%  $\text{MnO}_2$  reach the plateau later due to their uninfluenced electrochemical capacity, in accordance with its lower voltage that indicates a lower intrinsic electrode resistance due to an undamaged conductive network.

#### 4. Discussion

It is known that manganese oxides at the positive electrode enhance the proton diffusion [10] and may therefore improve the chargeability of the nickel hydroxide. Furthermore, and this is even more important, manganese oxides having an Mn oxidation state +4 are thermodynamically able to oxidize  $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$  (e.g.  $\beta\text{-Co}(\text{OH})_2 \rightarrow \beta\text{-CoOOH}$ ) as well as  $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+}$  with  $z > 2$  [6]. The latter could also be a relevant process because negative potentials may not only lead to a reduction of  $\beta\text{-CoOOH}$  but also to reduced nickel hydroxide which may be intrinsically inactive and difficult to charge.

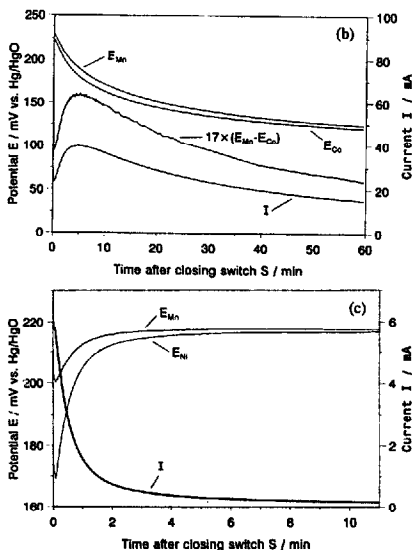
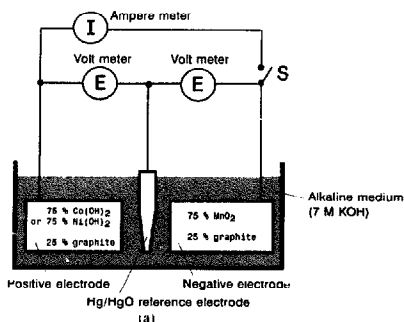


Fig. 3. (a) Experimental setup to demonstrate that  $\text{MnO}_2$  is able to oxidize  $\text{Co}(\text{OH})_2$  and  $\text{Ni}(\text{OH})_2$ . (b)  $\text{MnO}_2$  oxidizes  $\text{Co}(\text{OH})_2$  and its current and electrode potentials vs. time;  $E_{\text{Mn}}$  and  $E_{\text{Co}}$  denote the potentials of the  $\text{MnO}_2$  and  $\text{Co}(\text{OH})_2$  electrode, respectively. The enhanced potential difference  $E_{\text{Mn}} - E_{\text{Co}}$  is also shown. (c)  $\text{MnO}_2$  oxidizes  $\text{Ni}(\text{OH})_2$  and its current and electrode potentials vs. time.  $E_{\text{Mn}}$  and  $E_{\text{Ni}}$  denote the potentials of the  $\text{MnO}_2$  and  $\text{Ni}(\text{OH})_2$  electrode, respectively.

$\text{MnO}_2$  ( $\text{Mn}^{4+}$ ) was simply added to the positive electrode mixture as the starting additive component. Furthermore, it is thermodynamically possible to generate high-valent manganese oxides ( $\text{Mn}^{+6}$  and  $\text{Mn}^{+7}$ , i.e. soluble permanganates  $\text{MnO}_4^{2-}$  and  $\text{MnO}_4^-$ ) from  $\text{MnO}_2$  by electrochemical oxidation during the charging periods of the cycles. We assume that  $\text{MnO}_2$  and the solved permanganates operate differently in the following way, keeping in mind that both of the fol-

lowing processes may take place simultaneously with mutual influence.

MnO<sub>2</sub> is not only thermodynamically but also kinetically able to oxidize Co<sup>2+</sup> and Ni<sup>2+</sup>. This statement is supported experimentally as shown in Fig. 3(a)–(c). The experimental setup consisted of an MnO<sub>2</sub> electrode and a Co(OH)<sub>2</sub> or Ni(OH)<sub>2</sub> electrode, respectively, both immersed in 7 M KOH (Fig. 3(a)). The electrodes were made by mixing 1.5 g MnO<sub>2</sub>, Co(OH)<sub>2</sub> and Ni(OH)<sub>2</sub>, respectively, with 0.5 g graphite. The mixtures were pressed into buttons and covered with a nickel mesh. A spot-welded nickel metal was used as current collector. Before closing switch S (Fig. 3(a)–(c)) the open-circuit potentials were measured to be about +230, –230 and –110 mV versus Hg/HgO for the MnO<sub>2</sub>, Co(OH)<sub>2</sub> and Ni(OH)<sub>2</sub> electrode, respectively. After closing the circuit a current was observed. The existence of a current from the MnO<sub>2</sub> electrode to the Co(OH)<sub>2</sub> and Ni(OH)<sub>2</sub> electrode revealed a reduction of MnO<sub>2</sub> and an oxidation of Co(OH)<sub>2</sub> and Ni(OH)<sub>2</sub>. The time dependence of the current and of the electrode potentials was recorded (Fig. 3(b) and (c)). In order to understand the behaviour shown in Fig. 3(b) one has to take into consideration the following points. The occurrence of a current maximum is probably due to the successive penetration of oxidized and therefore conductive regions within the Co(OH)<sub>2</sub> (Co(OH)<sub>2</sub> is an electrical insulator). The relatively rapid decrease in MnO<sub>2</sub> electrode potential is due to its poor load capability. This was revealed by reducing a freshly prepared MnO<sub>2</sub> electrode with a current source ( $I = 40$  mA) against a nickel counter electrode, whereby a similar fast potential decay was observed. Compared with the thermodynamical Co<sub>3</sub>O<sub>4</sub>/Co<sub>2</sub>O<sub>3</sub> (Co<sup>2.67+</sup>/Co<sup>3+</sup>) potential of +90 mV versus Hg/HgO [6] the measured values are quite high (see Fig. 3(b)) and decrease in the course of time similar to that of the MnO<sub>2</sub> electrode potential. Oxidizing a freshly prepared Co(OH)<sub>2</sub> electrode with a current source ( $I = 40$  mA) against a nickel counter electrode revealed a similar potential decay. This observation indicates that the relatively high potential at the Co(OH)<sub>2</sub> electrode is probably an overvoltage phenomenon. The actual situation is certainly more complex as intimated so far, because there are several possible side reactions between the Mn and Co compounds and the electrolyte [6]. In contrast to Co(OH)<sub>2</sub> (Fig. 3(b)) the oxidation of Ni(OH)<sub>2</sub> (Fig. 3(c)) displays a less complicated behaviour. The small current and its fast decay suggests that the oxidation takes only place at the surface of the nickel hydroxide particles. The final potential of about +220 mV versus Hg/HgO indicates the presence of Ni<sup>3+</sup> with  $x > 2$  [6].

The excellent solubility of the permanganates is considered to be also advantageous to oxidize regions that are electrically isolated. This assumption is supported by the following experimental observation: KMnO<sub>4</sub> was solved in 7 M KOH

and the solution was separated in two parts. In one of these solutions Ni(OH)<sub>2</sub> powder was added whereas the second solution were left in its virginal state (violet colour) as the reference. We observed a darkening at the surface of the Ni(OH)<sub>2</sub> (indicating its oxidation) and an immediate change from violet (Mn<sup>7+</sup>) to green (Mn<sup>6+</sup>), in contrast to the reference solution where the colour remained unchanged within the observation time.

We would like to mention that the so-far presented considerations are certainly simplified and represent only selected aspects of the complicated processes that may take place at the positive electrode. These processes are not completely known and understood yet. For example, the possible role of compounds such as (Co,Ni)OOH [5] and (Co,Mn)OOH [11] has to be clarified.

#### Acknowledgements

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