

## ON THE ANOMALOUS BEHAVIOUR OF DEEPLY DISCHARGED, SEALED Ni-Cd CELLS

J. MRHA, M. MUSILOVÁ and J. JINDRA

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 102 00 Prague 10 (Czechoslovakia)*

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### Summary

Some sealed Ni-Cd cells on a deep, constant-current discharge show anomalous behaviour in that their voltage remains (after polarity reversal) in the range from  $-60$  to  $-260$  mV. This situation can sometimes persist for an unlimited time without any increase in the overpressure in the cell or of its voltage. A necessary condition for the appearance of this discharge voltage level is a discharge capacity reserve of the cadmium electrode and the presence of cadmium in the separator as a result of its migration from the negative to the positive electrode. The cadmium particles form bridges across the separator leading eventually to a short circuit, whereby the electrode reactions in the cell cease. This concept was substantiated by using separators impregnated with  $\text{Cd}(\text{OH})_2$ .

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### Introduction

The behaviour of sealed Ni-Cd cells during deep discharge is a problem which has not been satisfactorily solved. In a battery of series-connected cells, the cells usually differ somewhat in their capacity and quality; the cell with the minimum capacity breaks down first during deep discharge and its polarity is eventually reversed, leading to gassing. Gas starts to evolve from that electrode which is discharged first, thus limiting the cell capacity.

Sealed Ni-Cd cells are protected against the consequences of a deep discharge by a so-called antipolar admixture to the positive electrode [1], by charging the positive electrode prior to hermetic sealing of the cell [2 - 4], and by inserting auxiliary gas electrodes [5]. The first two methods of protection only lead to a delay in the hydrogen evolution but they do not ensure complete resistance of the sealed cells to the consequences of cell voltage reversal. The use of auxiliary gas electrodes is practical in the case of sealed cells for special applications, but not for general production, that is, not for small sized cells.

With commercial sealed cells therefore, cell reversal continues to be a constant problem. It was found that some sealed Ni-Cd cells showed anomalous behaviour on cell reversal, *i.e.*, even during a prolonged overdischarge no increase in cell overpressure was observed, the cell voltage not exceeding  $-300$  mV. This phenomenon was attributed to the possible presence of cadmium and/or its hydroxide in the separator due to migration of cadmium ions from the negative to the positive electrode [6]. We have studied this effect more closely in the present work.

## Experimental

Sealed D-size Ni-Cd cells of VRD type, (SAFT) were used containing plastic-bonded Cd electrodes and sintered nickel oxide electrodes in a coiled system [7]. Their capacity was 4.8 - 5.2 A h at the 5 h rate of discharge to 1.0 V. Cell reversal was achieved by discharging constantly at a current of 0.8 A.

To study the effect of the addition of  $\text{Cd}(\text{OH})_2$  into the separator,  $4 \times 7.5$  cm electrodes were cut from the original electrodes removed from the above mentioned cells. The positive electrode was sandwiched between two negative electrodes in a closely packed arrangement. The separator consisted of two layers of nonwoven polyamide fabric from the firm of K. Freudenberg (thickness 0.17 mm, density  $65.1 \text{ mg/cm}^2$ ). In some cases the separator was impregnated by dipping it into a saturated solution of  $\text{Cd}(\text{NO}_3)_2$ , removing the excess liquid, and then dipping it into a solution of KOH (density 1.3), which was renewed several times to prevent build up of nitrate ions in the separator, but a major portion of the  $\text{Cd}(\text{OH})_2$  precipitate was also removed.

Changes of overpressure within the cells were detected by measuring the cell height by means of a sensitive indicator; its variations,  $\Delta h$ , were due to deformation of the cell lid caused by the increasing overpressure.

## Results and discussion

Typical discharge curves for the sealed VRD Ni-Cd cells are shown in Fig. 1. The early parts of the curves, from the beginning up to zero V, are similar, *i.e.*, the cells all have practically the same capacity. However, after cell reversal, considerable differences are observed. Cell 1 shows an ill-developed voltage delay slightly below zero V followed by an abrupt increase of the negative terminal voltage. This is accompanied by an increase in the cell overpressure. By contrast, in cell 2 the terminal voltage became stabilized in the region of the delay corresponding to cell 1 until a cell voltage of about  $-0.16$  V was attained. When the deep discharge was interrupted for 73 h, and later for 20 h, no substantial change was observed, and the cell voltage finally reached a value of  $-80$  mV, which did not change even after several hours. The cell overpressure, indicated by the deformation of the lid, in-

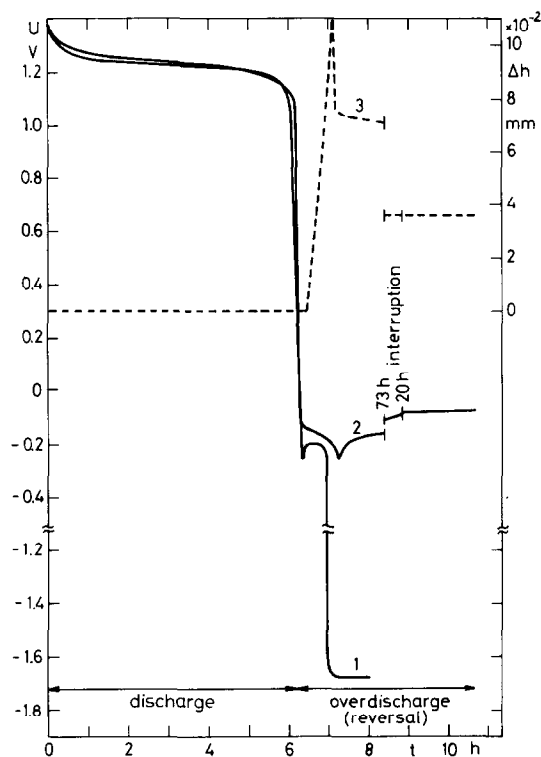


Fig. 1. Discharge curves of the sealed VRD cells. 1, cell 1; 2, cell 2; 3, variation with time of the overpressure in cell 2.

creased considerably when the voltage delay began to form. The variation with time of the overpressure during this interval resembles a mirror image of the voltage-time curve. The reason for this relation will be clear from the text below.

At the end of the reversal period, the lid of cell 2 was provided with an opening through which a Luggin capillary connected to an Hg/HgO reference electrode was inserted. The potentials of the electrodes were measured during reversal ( $i = 0.8$  A),  $E_{\text{Cd}} = -830$  mV,  $E_{\text{NiO}_x} = -910$  mV, and during the rest period (on open circuit),  $E_{\text{Cd}} = E_{\text{NiO}_x} = -871$  mV. This shows that the discharge (*i.e.*, oxidation) of the cadmium electrode in the closed cell continued during the voltage reversal, and that the nickel oxide electrode must have been responsible for the cell voltage attaining, transiently, more negative values than  $-200$  mV. The hydrogen evolved on this electrode during the first minutes of the reversal caused a rise in the overpressure within the cell. Immediately a distinct minimum of  $-260$  mV appeared on the  $E-t$  curve, followed by a voltage rise to more positive values, the cell height (the overpressure) decreased abruptly. After disconnecting the current, the cell voltage dropped quickly from  $-80$  mV to zero and both electrodes acquired a potential of  $-871$  mV (the rest potential of the partly discharged cadmium electrode).

Our results suggest that the active cadmium material was transferred in some sealed VRD cells through the separator towards the positive electrode, as assumed by other authors [6]. Since the cadmium electrode has a discharge reserve, hydrogen is evolved on the nickel oxide electrode during cell reversal, which initiates the formation of Cd dendrites growing through the separator and eventually reaching the cadmium electrode. If its potential is sufficiently negative (*i.e.*, if it is not completely discharged), conductive bridges are gradually formed between both electrodes until they become short-circuited and the electrode processes are stopped.

To support this explanation further, we placed a separator treated with cadmium hydroxide between two rectangular electrodes of dimensions  $4 \times 7.5$  cm taken from a VRD cell. The electrodes were fully charged, hence the negative ones had a discharge reserve. Their discharge  $E - t$  curves are shown in Fig. 2(a), from which the formation of the conducting cadmium bridges across the separator is apparent. At the beginning of the voltage reversal, hydrogen evolution at the nickel oxide electrode was detected, its potential surpassing transitorily the value of  $-1$  V; at the same time, metal bridges began to grow from the nickel oxide toward the cadmium electrode until both electrodes were short-circuited and the evolution of hydrogen ceased (the potential of the nickel oxide electrode was about  $-970$  mV). During subsequent charging, the bridges were oxidised on the positive electrode side within a few minutes and the short circuit was interrupted.

When the separator was replaced by a second containing no cadmium hydroxide, the potential of the nickel oxide electrode after the reversal rapidly reached the value for hydrogen evolution and no potential delay

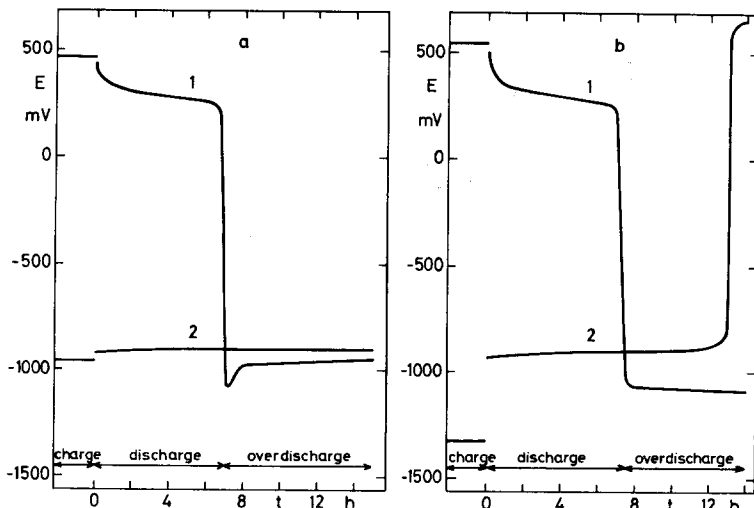


Fig. 2. Potential-time characteristics of the experimental Ni-Cd cells provided with (a), and without (b),  $\text{Cd}(\text{OH})_2$  separator treatment. 1, nickel oxide electrode; 2, cadmium electrode.

close to zero volts appeared (see Fig. 2(b)), evidence that no bridges across the separator were formed. Such a system in a sealed cell obviously would not withstand the consequences of a voltage reversal.

The question is whether the described phenomenon could be made use of in protecting the sealed cells against the noxious effect of a deep discharge. The main problem consists in interrupting the metal bridges during the time when the cell is in a more or less charged state. The cadmium content in the separator should obviously be as small as possible to prevent rapid self-discharge.

The results of measurements of the electrode potentials of an experimental cell, together with the voltage at the end of charging and discharging capacity to zero volts, are given in Table 1. A separator impregnated with  $\text{Cd}(\text{OH})_2$ , which after the 5th cycle was replaced with a separator free from cadmium was used. It is seen from these data that the presence of the  $\text{Cd}/\text{Cd}(\text{OH})_2$  system in the separator resulted in a lower voltage at the end of charging, compared with the cell containing the pure separator. This is due to lower absolute values of both electrode potentials. During charging, the cadmium bridges have, on the negative electrode side, a metallic character, whereas on the other side they are oxidised, and metallic cadmium is supplied from the cadmium electrode. Thus, we have to deal with a cadmium cycle between both electrodes similar to the oxygen cycle in sealed Ni-Cd cells. Owing to this cadmium cycle, there is only a slight evolution of oxygen at the positive electrode at the end of charging and no evolution of hydrogen at the negative electrode. The capacities obtained, together with the rapid self-discharge of the experimental cell with the separator impregnated with  $\text{Cd}(\text{OH})_2$ , suggest that the cadmium bridges are not affected during idling or discharging.

For practical applications it would be necessary to optimize the cadmium content in the separator, its thickness and porosity in order that the cadmium bridges may be effective during (cell) voltage reversal and the self-discharge may be sufficiently slow.

TABLE 1

Electrode potentials ( $E$ ), cell voltage ( $U$ ) at the end of charging, and discharge capacity ( $C$ ) to zero volts of experimental Ni-Cd cell

Cycle No.	$E_{\text{Cd}}$ (mV)	$E_{\text{NiO}_2}$ (mV)	$U$ (mV)	$C$ (mA h)
1	- 943	+473	1416	1046
2	- 967	+483	1450	976
3	- 971	+472	1443	940
4	- 971	+465	1436	362*
5	- 973	+461	1434	845
6	-1421	+555	1976	1134
7	-1323	+535	1858	1097*

\*Capacity after 72 h self-discharge.

## Conclusions

It has been substantiated that cadmium can migrate through the separator in sealed Ni-Cd cells toward the nickel oxide electrode. As soon as the potential of this electrode becomes sufficiently negative during deep discharge, electrically conducting cadmium bridges are formed. When their rate of formation at the cadmium electrode is higher than the rate of their reoxidation, the electrodes become short circuited at reversal of the cell voltage and the electrode processes are stopped. Thus, damage of the sealed Ni-Cd cell is prevented. A cadmium electrode discharge reserve against the positive electrode is a necessary condition for this behaviour. A higher cadmium content in the separator causes rapid self-discharge.

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