

## OXYGEN RECOMBINATION RATE ON PLASTIC-BONDED CADMIUM ELECTRODES DOPED WITH NICKEL(II) HYDROXIDE

S PETROVIČ, J. GARCHE and K WIESENER\*

*Department of Chemistry, Dresden Technical University, 8027 Dresden (G D R.)*

J MRHA and J JINDRA

*J Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague (C.S S R)*

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### Summary

It was found that the rate of reduction of oxygen on plastic-bonded cadmium electrodes doped with  $\text{Ni}(\text{OH})_2$  is highest when the added nickel amounts to 0.3%. If the active material is in prolonged contact with a solution of  $\text{NiSO}_4$  and then alkalized, its oxygen reduction activity is appreciably lowered, probably owing to a cementation reaction giving metallic nickel

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### Introduction

As was shown earlier [1 - 4], the recombination (reduction) of oxygen in hermetically sealed Ni-Cd accumulators is greatly hindered if 'so-called' plastic-bonded cadmium electrodes are employed. The use of a metal mesh contacting the gas side of the cadmium electrode [2], or the addition of active carbon into the active material [3], leads to an increased rate of oxygen reduction. On the other hand, the use of metal meshes complicates the manufacture of the accumulators, and the addition of active carbon gives rise to problems during overdischarge of the negative electrode, causing partial oxidation of the carbon material.

The addition of  $\text{NiSO}_4$  to the active material, which has been used for some time to stabilize the capacity of the negative electrode [4], causes an increase in the reduction rate of oxygen under certain conditions [5, 6]. A detailed study of this effect, and optimization of the amount of nickel compound added, forms the subject of the present work.

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\* Author to whom correspondence should be addressed

## Experimental

### *Measurements on 2 A h cells*

The construction and functioning of the 2 A h cells, and measurements of their internal pressure, have already been described [1 - 3]. The positive electrode, a commercial 2 A h pocket type, was placed between two, 2 A h, cadmium electrodes with a polyamide separator. The latter electrodes were of the plastic-bonded (rolled) type containing 5% Teflon [1 - 3, 5, 7] mixed with finely-dispersed, oxidized, cadmium powder, which are the basic material for commercial accumulators in the G.D.R. (composition about 80 - 90% CdO and 20 - 10% Cd). It contains about 0.3% Ni, introduced during the manufacturing process.

The active cadmium was doped with nickel. To increase the nickel content to 0.6%, 50 ml of 60%  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  solution was added to 1 kg of the cadmium material, which was mixed thoroughly at 80 °C, before 45 ml of 20% NaOH (density 1.22 g cm<sup>-3</sup>) were added 15 min later. Optimization of the Ni content was achieved by changing the quantity of the solutions. The molar ratio of  $\text{NiSO}_4$  to NaOH was constant, except in one case when it was increased by a factor of 5. The density of the NaOH solution varied from 1.1 to 1.35 g cm<sup>-3</sup>. Another procedure consisted of alkalinizing the active material in an excess of 30% KOH (density 1.29 g cm<sup>-3</sup>) after assembling the cell.

### *Measurements on model electrodes*

Fine, nickel-free cadmium powder, prepared by cementation of a solution of 150 g l<sup>-1</sup> of  $\text{CdCl}_2$  and 55 g l<sup>-1</sup> of HCl with magnesium, was pressed from both sides onto an iron mesh at 10 MPa to form a 2.6 cm dia., 3 mm thick disc with 350 mA h capacity (at 5 h discharge rate). This was placed in a commercial corrosion measuring cell, KMZ-1 (Forschungsinstitut Meinsberg, G.D.R.), with a solution of 7 M KOH (density 1.3 g cm<sup>-3</sup>). Measurements were carried out at 25 °C and potentials are referred to an Hg/HgO reference electrode in the same electrolyte ( $E = +0.013$  V against SHE).

Potentiodynamic measurements were made using an X-Y recorder. Five minutes after charging the electrode, it was once more polarized cathodically at a sweep rate of 0.02 V s<sup>-1</sup> beginning from the stationary potential.

To measure the gas volume after charging the electrode, the measuring cell was hermetically closed and connected with a gas burette. To increase the reduction rate of oxygen, only one half of the electrode was immersed in the electrolyte. The temperature was kept at 25 ± 2 °C by an air thermostat.

## Results

### 2 A h cells

The rate of oxygen reduction can be characterized [1] by the equilibrium overpressure,  $\Delta p$ , as a function of the charging current, shown in Fig 1 for cadmium electrodes with different nickel contents. It can be seen that the  $\Delta p$ - $I$  curve (d) for an electrode containing 0.3% Ni lies close to that for the pocket type electrode (e). The, surprisingly, little pronounced  $\Delta p$ - $I$  dependence for non-doped electrodes reported previously (*e.g.*, ref. 1, Fig. 4) may be attributed to a different quality of the Cd active material, presumably to its different basic nickel content

The gas overpressure,  $\Delta p$ , as a function of the nickel content at 750 mA charging current is shown graphically in Fig 2. It can be seen that the rate of oxygen reduction is greatest when the active material contains 0.3% added Ni, and the same conclusion can be drawn from Fig. 1 at different charging currents.

The influence of the alkalization step on the  $\Delta p$ - $I$  curves is shown in Fig. 3. It can be concluded that changing the concentration of the NaOH solution (the quantity of NaOH being kept constant) added 15 min after the addition of  $\text{NiSO}_4$  has no marked effect on the rate of oxygen reduction.

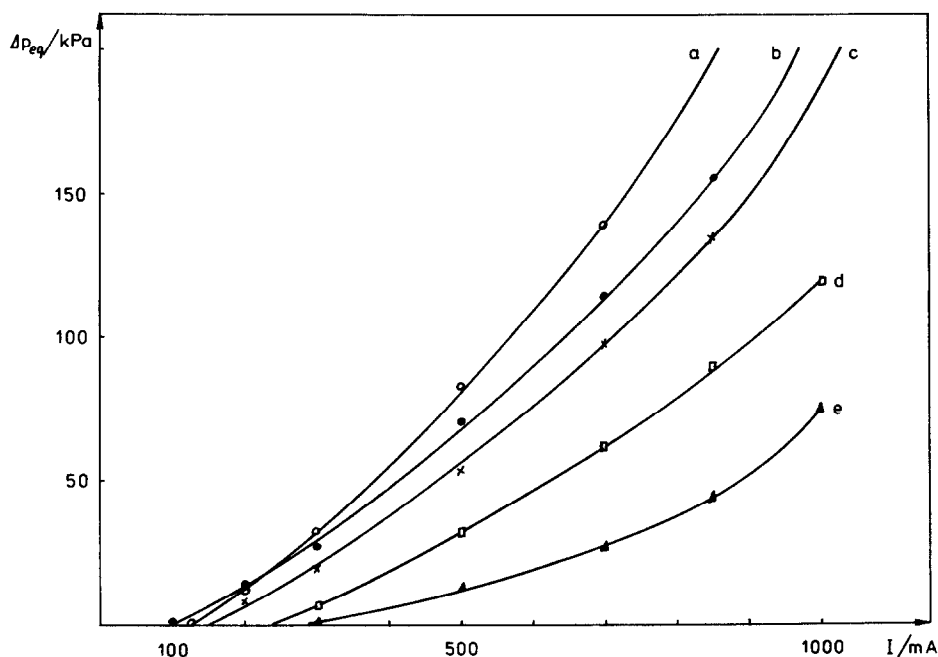


Fig 1 Equilibrium overpressure,  $\Delta p_{eq}$ , as a function of charging current,  $I$ , for various Cd electrodes Added nickel (II) content (a) none, (b) 1.2%, (c) 0.6%, (d) 0.3%, (e) none, (a) - (d) plastic-bonded electrodes, (e) pocket-type electrode

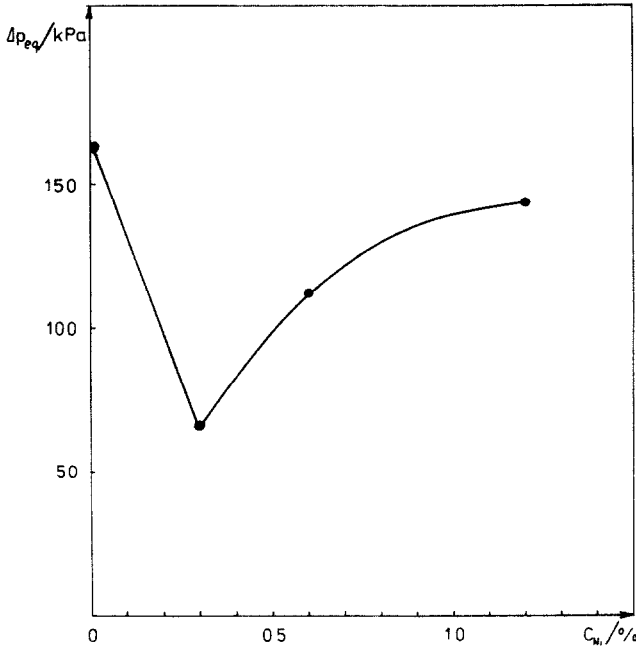


Fig 2 Equilibrium overpressure,  $\Delta p_{eq}$ , for Cd electrodes as a function of the added nickel(II) content at 750 mA charging current

When the electrode active material is alkalized only after assembling the cell (after a longer time), however, its oxygen reduction activity is appreciably lower

### Model electrodes

#### Voltammetric measurements

Typical voltammograms for a cadmium electrode are shown in Fig. 4 both in the absence and in the presence of oxygen. The cathodic current in the presence of oxygen,  $I_{OE}$ , is given by

$$I_{OE} = I_{O_2,R} + I_{Cd,R} + I_{H_2} \quad (1)$$

where  $I_{O_2,R}$  is the current corresponding to the reduction of oxygen,  $I_{Cd,R}$  corresponds to the reduction of  $Cd(OH)_2$ , and  $I_{H_2}$  corresponds to the evolution of hydrogen. When the electrolyte is deoxygenated with nitrogen or argon, the cathodic current,  $I_{DOE}$ , is given by

$$I_{DOE} = I_{Cd,R} + I_{H_2} \quad (2)$$

The rate of oxygen reduction can be characterized by the maximum reduction current, which is measured in the potential range from  $-1.00$  to  $-1.03$  V. The corresponding current due to oxygen reduction

$$I_{O_2,R} = I_{OE} - I_{DOE} \quad (3)$$

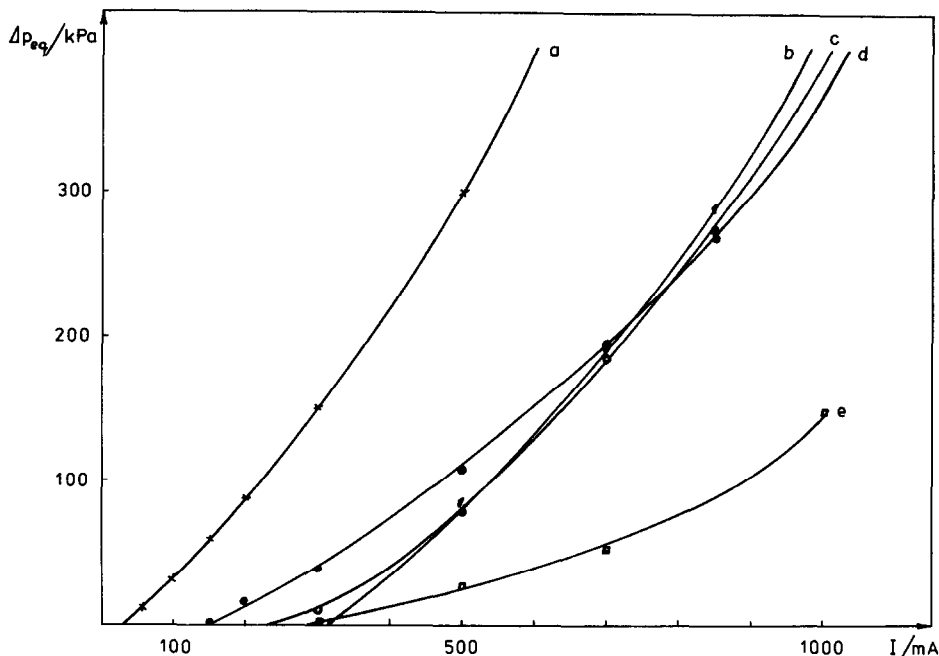


Fig 3 Equilibrium overpressure,  $\Delta p_{eq}$ , for Cd electrodes with different times of alkalization, and for a pocket-type electrode, as a function of the charging current,  $I$  (a) Alkalization with 30% KOH after assembling the cell, (b) alkalization with NaOH ( $\rho = 1.1 \text{ g cm}^{-3}$ ) immediately after impregnation with  $\text{NiSO}_4$ , (c) as (b), but  $\rho = 1.22 \text{ g cm}^{-3}$ , (d) as (b), but  $\rho = 1.35 \text{ g cm}^{-3}$ , (e) pocket-type electrode. The number of moles of NaOH for electrodes (b) - (d) was constant.

is shown graphically in Fig. 5 as a function of the nickel content. Here also, it can be seen that the maximum reduction rate of oxygen corresponds to 0.3% of added nickel.

In addition to varying the concentration of NaOH in the alkalization step, the quantity of the solution and the time of its addition were also changed. If various quantities of NaOH are added immediately after the addition of  $\text{NiSO}_4$ , the peak current remains approximately the same (Fig. 6, electrodes a, b, and c). On the other hand, when the NaOH solution is added a long time after the addition of  $\text{NiSO}_4$ , the current due to oxygen reduction calculated from eqn. (3) is considerably decreased (electrode d). This may be explained in terms of an increase of the current due to the reduction of  $\text{Cd}(\text{OH})_2$ ,  $I_{\text{Cd,R}}$  resulting from increased self-discharge during idling, as well.

X-ray diffraction data for electrodes a - d (Fig. 6) revealed no essential differences, whereas the BET surface area,  $S$ , is lower in the case of electrode d. The active material contained 0.3% of added Ni in each case; the relevant data are given in Table 1.

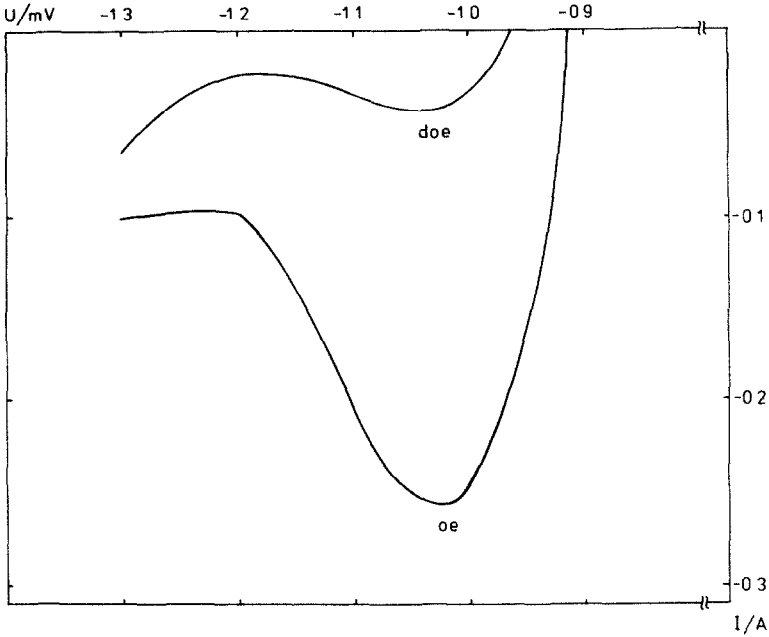


Fig 4 Voltammetric curves for a Cd electrode with 0.3% added Ni(II) in air-saturated electrolyte (oe) and de-aerated electrolyte (doe). Sweep rate  $20 \text{ mV s}^{-1}$

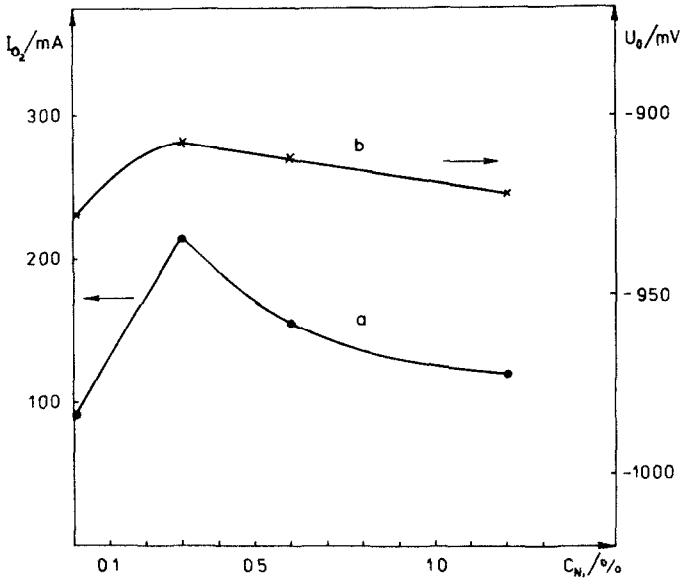


Fig 5 Calculated oxygen reduction current  $I_{O_2, \text{Red}}$  at  $-1.02 \text{ V}$  in voltammetry at  $20 \text{ mV s}^{-1}$  (a), and equilibrium potential of Cd electrodes (b), as a function of the Ni(II) content added to the active material

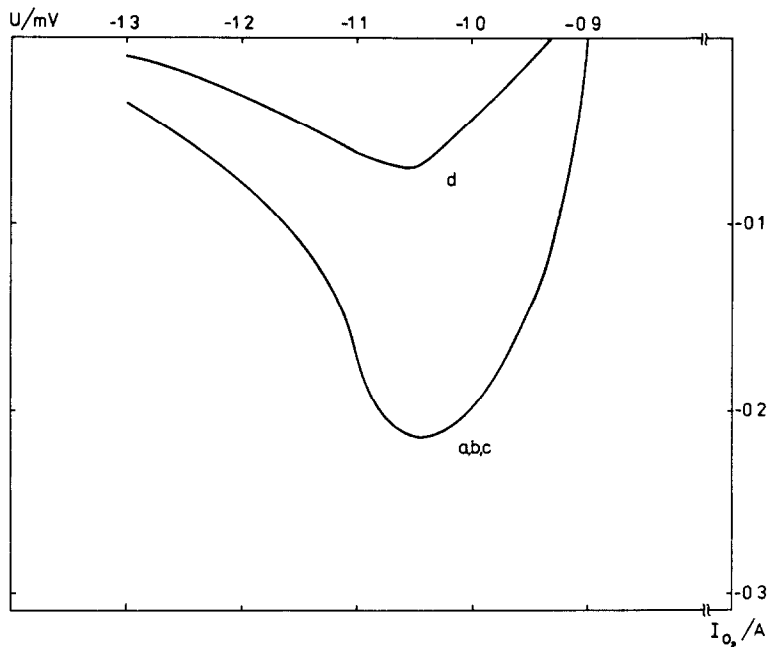


Fig 6 Calculated oxygen reduction current  $I_{O_2,Red}$  as a function of the potential (in voltammetry at  $20 \text{ mV s}^{-1}$ ) for Cd electrodes with 0.3% added Ni(II) (a) Alkalization immediately with NaOH ( $\rho = 1.22 \text{ g cm}^{-3}$ ), mol ratio of NaOH to  $\text{NiSO}_4$  0.62, (b) as (a), but mol ratio 3.1, (c) alkalization immediately with KOH ( $\rho = 1.29 \text{ g cm}^{-3}$ ), mol ratio 24.2, (d) as (c), but alkalization 65 h after impregnation with  $\text{NiSO}_4$

TABLE 1

BET surface areas of Cd active masses with 0.3% of added Ni(II), alkalinized with different alkali contents at different times. Electrode a, b, c, d, see legend to Fig 6

Electrode	a	b	c	d
$S (\text{m}^2 \text{ g}^{-1})$	2.5	2.4	2.4	1.2

#### *Measurements of stationary potential*

The stationary potential of the electrode is another characteristic of the rate of oxygen reduction (Fig. 5). In a deoxygenated solution, a mixed potential is established corresponding to the anodic and cathodic reactions



In 30% KOH, the system is thermodynamically stable at 7.3 kPa partial pressure of hydrogen

In the presence of oxygen, the mixed potential is determined also by the reduction of oxygen (the second cathodic partial reaction). This leads to the formation of a local corrosion current, causing a shift of the stationary potential to more positive values. The shift is largest at the optimum content of  $\text{Ni}(\text{OH})_2$ , since in this case the reduction of oxygen is least hindered.

#### *Measurements of the gas volume*

The rate of oxygen reduction was followed by measurement of the decrease of the volume of oxygen in contact with half-immersed electrodes. To minimize the effect of hydrogen evolution, the electrode was kept at the stationary potential. The  $\Delta V-t$  dependences for electrodes with different contents of nickel are shown in Fig. 7. Here, also, it is seen that the rate of oxygen reduction is maximum with 0.3% added nickel. Since the volume of oxygen was relatively large, the measurement proceeded at almost constant pressure, and the decreasing consumption of oxygen with the time may be attributed to coverage of the electrode with  $\text{Cd}(\text{OH})_2$  as a result of reaction (4). After 5 h reaction time, the capacity of the electrode containing 0.3% added Ni decreased by 10% and it can be seen from Fig. 8 that the rate of oxygen reduction decreases with increasing discharge state. Nevertheless, the reduction of oxygen proceeded even on a fully discharged Cd electrode (with 0.3% added Ni), although relatively slowly; and the same effect was observed on other electrodes doped with nickel, whereas with nickel-free electrodes, the consumption of oxygen was zero. It is concluded that fully discharged, Ni-doped electrodes have some small part of the cadmium sur-

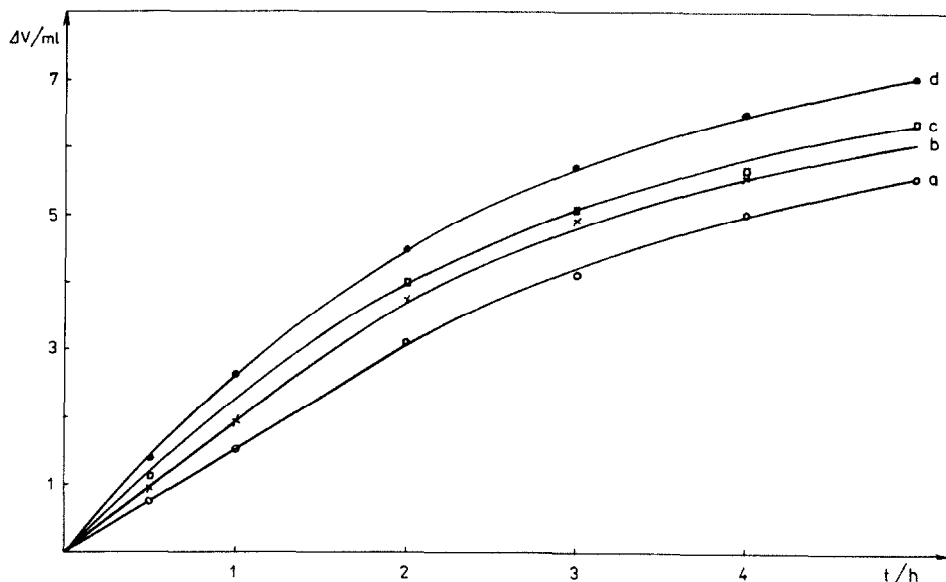


Fig 7 Decrease of oxygen volume,  $\Delta V$ , as a function of reaction time,  $t$ , for half-immersed Cd electrodes with added Ni(II) content (a) none, (b) 1.2%, (c) 0.6%, (d) 0.3%



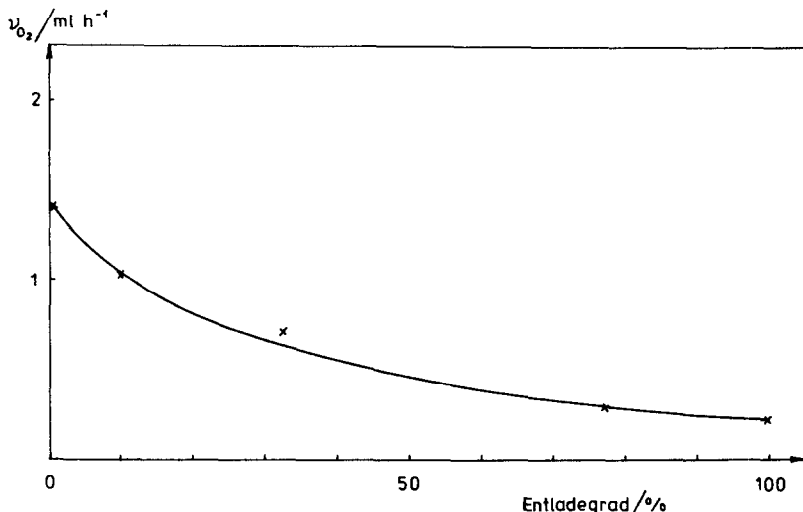


Fig 8 Rate of oxygen consumption  $\nu_{O_2}$  as a function of the discharge state (Entladegrad) for a half-immersed Cd electrode with 0.3% added Ni(II) after 5 h idling

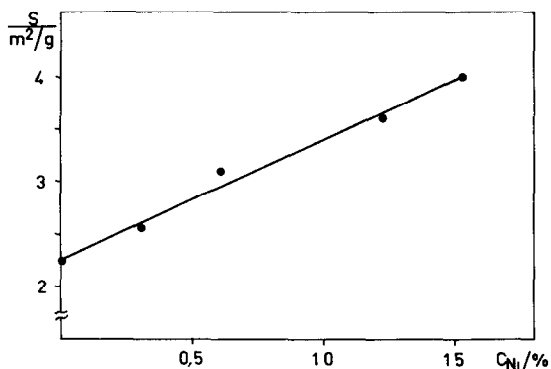


Fig 9 BET surface area,  $S$ , as a function of added Ni(II) content,  $C_{Ni}$ , of non-pressed active material

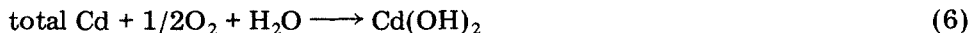
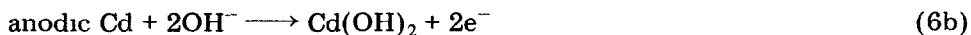
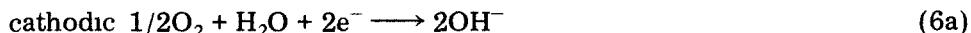
face still accessible for oxygen and electrolyte, whereas no such surface is available on the non-doped electrodes. This residual Cd surface does not contribute to the electrode capacity, probably because of an ohmic resistance.

As expected, a decrease of the reduction rate leads to a drop of the stationary potential with time. For a cadmium electrode with 0.3% added Ni, the stationary potential drop was 10 mV after 5 h idling.

The BET surface area of the non-pressed active material (after alkalization with NaOH) increases linearly with the nickel hydroxide content, as shown in Fig 9.

## Discussion

The open circuit reduction of oxygen proceeds by the following corrosion mechanism:



This is supported by the shift of the stationary potential of the cadmium electrode towards positive values with the addition of oxygen.

The cathodic step is rate-determining, because the anodic step has a very high exchange current density. In the overcharge period the cathodic step reflects the total reaction.

The oxygen reacts on the metallic Cd and not on the  $\text{Cd}(\text{OH})_2$ , which is a bad electron conductor. The distribution of Cd and  $\text{Cd}(\text{OH})_2$  in the electrode is not uniform, since  $\text{Cd}(\text{OH})_2$  is electrochemically reduced more adjacent to the current collector,  $i_e$ , in the centre of the electrode. Thus, the outer regions of the porous negative electrode serve as an overcharge reserve (Fig. 10). The transport of oxygen to the Cd particles is slowed down by the  $\text{Cd}(\text{OH})_2$  layer. Therefore, an unpretreated, plastic bonded Cd electrode cannot be used in sealed Ni-Cd cells. To do so requires that oxygen transport to the inner part of the electrode be improved. A higher porosity of the active mass on the basis of structure refining contributes to it. This is achieved by the alkaline  $\text{NiSO}_4$  activation as the BET values (Fig. 9) show.

About 50% of the surface increase is due to the specific amount of  $\text{Ni}(\text{OH})_2$  ( $49 \text{ m}^2 \text{ g}^{-1} \text{ Ni}(\text{OH})_2$ ), the residual 50% is the result of a lesser

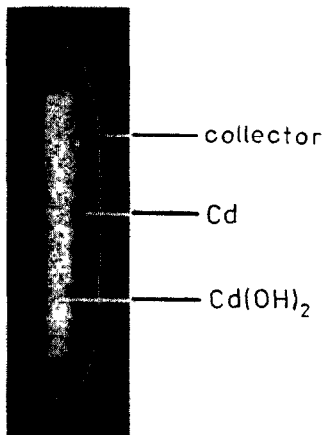


Fig 10 Cross section of the charged Cd electrode of a 225 mA h button cell

refinement of the  $\text{Cd}(\text{OH})_2$  crystals due to the crystal nucleus effect of  $\text{Ni}(\text{OH})_2$ . Increasing the  $\text{Ni}(\text{OH})_2$  concentration causes the structure of the active mass to be still finer (see Fig. 9). The simultaneous increase in the amount of finer pores, which participate to a lesser extent only in the transport of oxygen, leads to a decreased rate of oxygen reduction. Thus, there must be an optimum  $\text{Ni}(\text{OH})_2$  content, which has been found to be 0.3% Ni. It cannot be excluded that a modification of the structure of  $\text{Cd}(\text{OH})_2$ , which includes metallic Cd, makes the outer part of the electrode partially effective and supports some oxygen reduction in the sense that the diffusion of oxygen increases in it, as described by Avilova *et al* [10].

As may be seen from Fig. 6, the time delay between the addition of  $\text{NiSO}_4$  and alkalization has an extremely important influence. When the negative active material is in contact with the  $\text{NiSO}_4$  solution, deposition (cementation) of metallic Ni on cadmium takes place, since the standard potentials are

$$E^0(\text{Cd}/\text{Cd}^{2+}) = -0.403 \text{ V}, E^0(\text{Ni}/\text{Ni}^{2+}) = 0.250 \text{ V}$$

The Cd metal in the commercial active material is covered with an hydroxide layer, which, according to the literature [8, 9] decreases the rate of the cementation reaction. This layer is partially dissolved in contact with the slightly acidic  $\text{NiSO}_4$  solution (pH = 5.1).

If, after  $\text{NiSO}_4$  addition by means of alkalization, the pH value is increased instantaneously, the dissolution of  $\text{Cd}(\text{OH})_2$ , and thus the Ni cementation, remains very small (no Ni signals have been found by X-ray measurement). If alkalization occurs only after 65 h, then most of the nickel has been converted into the metallic form, as shown by our X-ray measurements.

The catalytic effect of the metallic Ni plays only a small rôle, since the Cd electrode potential is very negative ( $E \leq -0.90 \text{ V}$ ). This is confirmed by the fact that the rate of oxygen reduction becomes a first approximation, independent of the quality of the current collector material (copper, nickel, steel mesh).

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