

PROTECTION OF SEALED NICKEL-CADMIUM CELLS AGAINST CELL VOLTAGE REVERSAL II. INFLUENCE OF THE SEPARATOR ON THE FORMATION OF CADMIUM BRIDGES

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Summary

After studying three types of polyamide fabric, each with different physical parameters and different properties, as separators in an alkaline electrolyte, two widely differing materials were selected. These were evaluated by scanning electron microscopy both before and after the chemical deposition of cadmium hydroxide ($\text{Cd}(\text{OH})_2$). Their physical parameters were correlated with their efficiency in the formation of protective cadmium bridges in sealed nickel-cadmium accumulators during deep discharge accompanied by voltage reversal. Two types of sealed accumulators were employed with differing electrode geometry and interelectrode distance, which was shown to be related to the $\text{Cd}(\text{OH})_2$ content of the separator.

Introduction

The behaviour of sealed Ni-Cd accumulators and especially the formation of cadmium bridges in the separator during deep discharge has been described earlier [1, 2]. These bridges can be utilized to protect the accumulator from the harmful consequences of deep discharge. The conditions under which they provide protection were specified on the basis of experiments using sintered Ni-Cd prismatic, sealed cells of 0.6 A h capacity (limited by the positive electrode). The results showed that:

(1) Both electrodes must contact the separator uniformly over their entire surface and must maintain an even thickness during operation, especially in the central zone. Therefore, sintered electrodes proved to be most satisfactory.

(ii) The electrode-separator system must be subjected to at least one preliminary cycle in an excess of electrolyte, causing a redistribution of cadmium in the separator allowing the growth of cadmium dendrites from the positive to the negative electrode

(iii) The cell capacity must be limited by the positive electrode, which can be polarised during overdischarge to a negative potential sufficient to cause reduction of $\text{Cd}(\text{OH})_2$ to metallic cadmium in the adjacent separator layer. The cadmium dendrites should not be oxidised (hence, disrupted) on the cadmium electrode, whose potential, therefore, should not become positive.

(iv) The reliability of the cadmium bridges depends on the number and thickness of the separator layers and on the content of $\text{Cd}(\text{OH})_2$ in the separator.

Experimental

In the present series of experiments the effect of the addition of $\text{Cd}(\text{OH})_2$ to the separator was first studied using a test cell with 4×7.5 cm sintered electrodes [2]. The separator was either Viledon (K. Freudenberg, FRG), Kasilon (Hedva, Moravská Třebová, CSSR), or GLZ fabric (used by Grubenlampenwerke Zwickau, GDR). Their wettability by the electrolyte (1.3 g cm^{-3} KOH solution) was determined on 8.7×8.7 cm samples, which were weighed in the dry state, and after soaking for 24 h in electrolyte and standing for 1 h in air on a polyamide net. The cells were then charged and discharged in an excess of electrolyte at a current of 200 mA, sealed cells were charged at 70 mA and discharged at 200 mA.

Further measurements were done on cylindrical cells of 225 mA h capacity with sintered, rolled electrodes. The cell components, except for the separator, were from the commercial 225 mA h cylindrical cell (k.p. Bateria Slaný, CSSR). The dimensions of the positive electrode were 1.8×5.2 cm and those of the negative electrode 1.8×7.0 cm. One or two layers of the Viledon separator were employed. The electrodes were rolled into a metal cylindrical case of 1.4 cm dia. and 2.4 cm height. After a preliminary formation cycle in an excess of electrolyte the cell was closed with an insulated lid by the hemming technique. An Hg/HgO reference electrode was used in the former case, and the terminal voltage was measured in the latter. The charging current was 25 mA and the discharging current 120 mA in both cases.

Impregnation of the separators with a solution of CdSO_4 and determination of the Cd content has been described previously [2]. The physical structure of 0.6×0.6 cm samples of the separators either prior to, or after, impregnation was studied by scanning electron microscopy following coating with an evaporated gold layer.

Experiments were also carried out with cells in which the separator was impregnated with $\text{Cd}(\text{OH})_2$ after the electrode, with the separator, had been

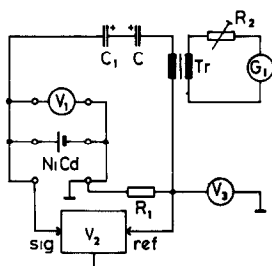


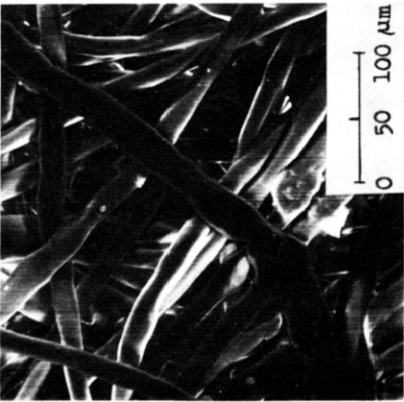
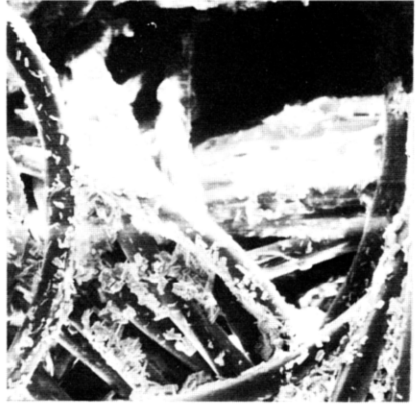
Fig 1 Diagram of the electrical circuit used in impedance measurements of Ni-Cd cells

rolled and inserted into the cell case. A solution of CdSO_4 of known concentration was introduced into the cell and after about half-an-hour, an excess of the alkaline electrolyte was added: this was then exchanged several times for a new one. The cells were thus subjected to formation in an excess of electrolyte. The excess electrolyte was then removed and the cell hermetically sealed

The a.c. impedance of cylindrical 225 mA h cells was measured according to the method of ref. 3, the diagram of the electrical circuit used is shown in Fig. 1. The high precision resistor R_1 , was set at 100Ω to give an ohmic voltage loss of 1 V at an a.c. current of 10 mA which was chosen to prevent deterioration of the protective cadmium bridge. The capacitors, C_1 and C_2 ($7 \times 10\,000 \mu\text{F}$ in parallel), prevent the cell from discharging through the low resistance of R_1 in series with the 1.1 isolating transformer, Tr, which, together with the calibrated variable resistance, R_2 , and signal generator, G_1 , controls the measuring current. The latter was chosen according to the voltage on R_1 indicated by the voltmeter, V_3 , at the frequency used. Voltmeter, V_1 , indicated the cell voltage. The a.c. voltage on R_1 served as reference signal for the lock-in amplifier, V_2 , used to measure the real and imaginary parts of the impedance. The frequency range was 20 Hz to 10 kHz and the measurements were repeated after several hours to check their reproducibility.

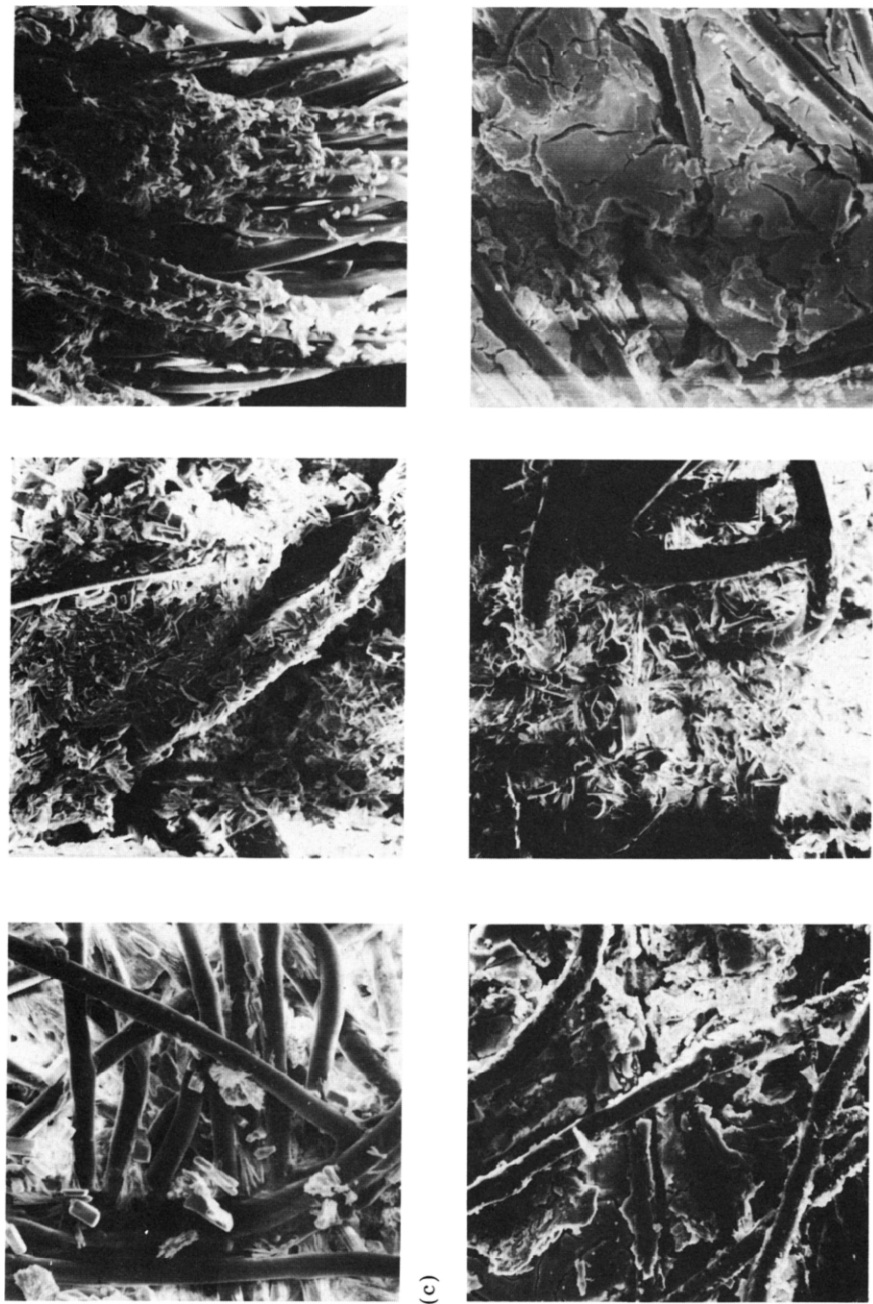
Results and discussion

Preliminary measurements indicated that the formation and function of the Cd bridges depended on the physical structure of the $\text{Cd}(\text{OH})_2$ impregnated separator. We used a non-woven fabric, Viledon, a woven fabric, Kasilon, made from crumpled fibres, and a common woven fabric, GLZ, the properties of which are given in Table 1. The GLZ fabric is the thickest and has the lowest porosity, whereas Viledon is the thinnest and has the highest porosity. Kasilon has the highest and Viledon the lowest wettability. With respect to the pore volumes, the approximate quantity of electrolyte on the surface of each of the fabrics was: 36% for Viledon, 56% for GLZ, and 64% for Kasilon. Kasilon retains a relatively large quantity of electrolyte on



(a)

(b)



(d)

Fig 2 SEM microphotographs Row a, pure separators, b, the lowest Cd(OH)₂ content (0.19 - 0.33 mg Cd cm⁻²), c, the medium Cd(OH)₂ content (0.63 - 1.72 mg Cd cm⁻²), d, the highest Cd(OH)₂ content (2.86 - 8.89 mg Cd cm⁻²)

TABLE 1

Physical parameters and wettabilities (in KOH solution) of separator materials

Parameter	Separator material		
	Viledon	Kasilon	GLZ
Thickness (cm)	0 012	0 022	0 025
Square weight (g cm^{-2})	0 0056	0 0107	0 0138
Apparent density (g cm^{-3})	0 466	0 486	0 552
True density (g cm^{-3})	1 16	1.16	1 15
Porosity (%)	60	58	52
Specific wettability (g g^{-1})	2 5977	4 3527	3 0434
Square wettability (g cm^{-2})	0 0149	0 0469	0 0382
Volume wettability (g cm^{-3})	1 24	2 13	1 53

its outer surface due to the special treatment of the fibres and their processing into the form of the final product. By contrast, Viledon retains a substantial quantity of the electrolyte in the interior of its structure and, therefore, holds it more firmly.

The structure of the separators and the distribution of $\text{Cd}(\text{OH})_2$ in them is well observed in the scanning electron microphotographs, Fig. 2, row (a) (all photographs are at $\times 210$ magnification with 16 kV). The GLZ fabric contains oriented, compact bundles of fibres, therefore its structure is more compact, whereas the fibres in Viledon are randomly distributed, so that the distribution of the electrolyte in it is more uniform. The Kasilon fabric has a very articulate outer surface, facilitating adhesion of the electrolyte after withdrawal into the air.

The distribution of the precipitated $\text{Cd}(\text{OH})_2$ can be seen from Fig. 2, rows (b) - (d). At the lowest content of $\text{Cd}(\text{OH})_2$ (row (b)), its distribution is most uniform in Viledon; agglomerates of $\text{Cd}(\text{OH})_2$ tend to form in the GLZ fabric, and especially in Kasilon, which may be a result of their peculiar structure. This tendency becomes more pronounced with increasing $\text{Cd}(\text{OH})_2$ content (row (c)), while it is absent in the case of Viledon. At the highest cadmium content (row (d)), the fibres of Kasilon or GLZ cease to be distinguishable but the fibres of Viledon are still visible. The $\text{Cd}(\text{OH})_2$ excess on Kasilon or GLZ is apparently preferentially precipitated on their surfaces and is apt to fall off during handling. This "free" $\text{Cd}(\text{OH})_2$ may possibly impair the lifetime of the cell.

The above findings suggest that Viledon is the most suitable support for the electrolyte and the $\text{Cd}(\text{OH})_2$. This conclusion was substantiated by the results obtained with prismatic test cells.

Electrochemical tests were carried out with cells containing 1 - 3 layers of either Kasilon or Viledon. The voltage-time curve for an open, prismatic cell of 0.6 A h capacity with an excess of electrolyte, recorded after voltage reversal, is shown in Fig 3. Protective Cd bridges are apparently formed in the case of Viledon at a cadmium content in the separator as low as 11 mg.

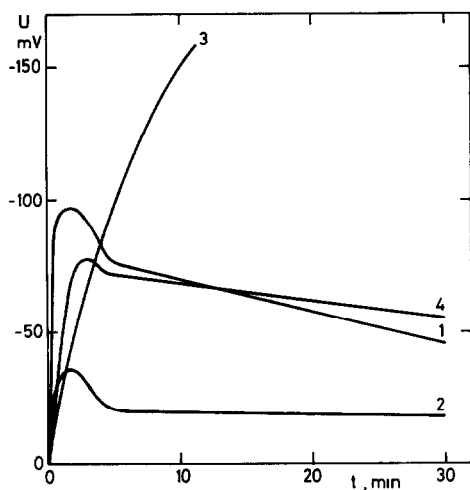


Fig 3 Discharge curves after cell voltage reversal Prismatic 0.6 A h vented cells, discharge current 200 mA Separator and Cd loading 1, Viledon, 11 mg, 2, Viledon, 582 mg, 3, Kasilon, 42 mg, 4, Kasilon, 66 mg

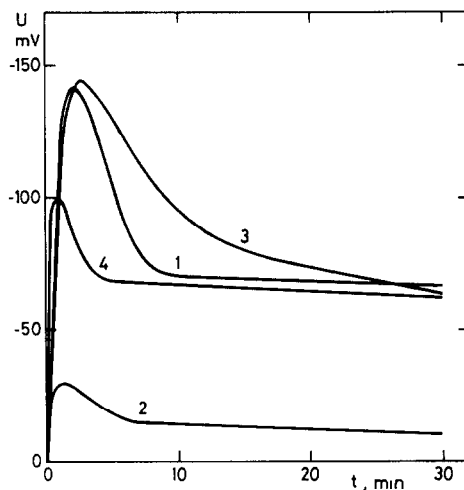


Fig 4 Discharge curves after cell voltage reversal Prismatic 0.6 A h sealed cells, discharge current 200 mA Separator and Cd loading 1, Viledon, 20 mg, 2, Viledon, 582 mg, 3, Kasilon, 66 mg, 4, Kasilon, 176 mg

A much higher quantity of cadmium (580 mg) only causes a shift of the voltage-time curve to lower negative values by about 50 mV. This can be attributed to a reduction in the internal resistance through the formation of a higher number of Cd bridges. In the case of Kasilon, at least 62 mg of Cd per separator is necessary to ensure the formation of Cd bridges. This can be related to differences between the two fabrics, discussed above.

In an hermetically-sealed cell operating under electrolyte-starved conditions and using the Viledon separator, only 20 mg of Cd is sufficient to ensure the formation of Cd bridges (Fig. 4).

In type 225 cylindrical cells using Viledon as much as 87 mg of Cd per separator was necessary for the formation of bridges. This can be attributed to the less compact cell construction (rolled electrode system), which does not ensure uniform contact over the entire surface (point (1) in Introduction). (With prismatic 0.6 A h cells, close packing was achieved by inserting insulation foils between the electrodes and the cell case prior to the formation cycle with excess electrolyte.)

The capacity of type 225 cells with excess electrolyte reached 260 mA h, and cadmium bridges were formed in a single layer of Viledon separator containing 80 mg of Cd. (With two separator layers, the bridges were very "weak" even when the Cd loading was increased to 150 mg.) After hermetically sealing the cells, their capacities were 212 - 236 mA h. Cadmium bridges were formed reliably, but the self-discharge was up to 35% after 120 h, evidence of separator overloading with cadmium. On the other hand, the

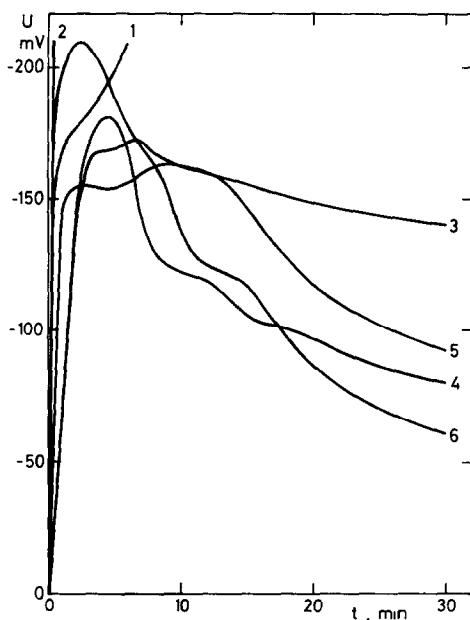


Fig 5 Discharge curves after cell voltage reversal Cylindrical 225 mA h sealed cells with Viledon separator, discharge current 120 mA Deep discharge cycle number and Cd loading 1 1, 0 mg, 2 5, 0 mg, 3 1, 87 mg, 4 4, 87 mg, 5 1, 137 mg, 6 3, 137 mg

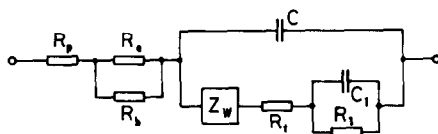


Fig 6 Equivalent circuit diagram of a Ni-Cd cell

self-discharge of the experimental prismatic 0.6 A h cells containing only 30 - 40 mg of Cd per separator was 15 - 20% after 120 h.

The parameters of cells doped with $\text{Cd}(\text{OH})_2$ in the assembled state were essentially the same as in the preceding case; their capacities were in the range 214 - 223 mA h. Here, also, a single separator layer was necessary for the reliable formation of Cd bridges. The terminal voltage of type 225 sealed cells after voltage reversal is shown graphically in Fig. 5. Curves 1 and 2 refer to commercial cells. Curve 1 indicates that the nickel oxide electrode reached the hydrogen evolution potential during the first 6 min of deep discharge, while the cadmium electrode was in the last stage of discharge, its potential being shifted toward evolution of oxygen. After five charge-discharge cycles, the initial difference between the capacities (12 mA) was eliminated, resulting in an abrupt shift of the terminal voltage below -0.2 V (curve 2). Curves 3 and 4 correspond to cells with 87 mg of Cd per separator in the first and fourth cycle, respectively. Their course, and relative position, indicate the formation of protective Cd bridges which improve on cycling (internal resistance decreases). The same can be said about curves 5 and 6 corresponding to a cadmium loading of 137 mg per separator, these are shifted nearer to zero terminal voltage, indicating the formation of still more efficient Cd bridges (the internal voltage losses are correspondingly lower).

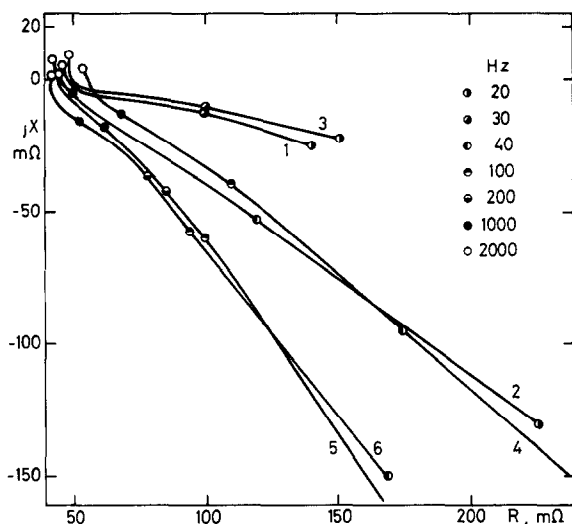


Fig 7 Complex plane impedance plots for different sealed 225 mA h cells 1, cell 1, stored 2 d after charging, 2, cell 1, 2 h after discharging to 1 V cut-off voltage, 3, cell 2 immediately after charging, 4, deeply discharged cell 2 with protective Cd bridges, 5, deeply discharged cell 3 with protective Cd bridges, 6, deeply discharged cell 3 immediately after disrupting the Cd bridges by 50 mA charging current Cell 1 is a commercial product, cell 2 has a separator with 87 mg Cd loading (impregnation prior to assembling the cell), cell 3 has 170 mg Cd loading (impregnation after assembling the cell)

Impedance measurements were carried out on type 225 cylindrical cells to detect the formation of protective Cd bridges. The cell can be represented by a modified equivalent diagram [4] shown in Fig. 6, where R_e corresponds to the resistance of the electrolyte in the separator, C is the capacity of the electrode double layer, R_t is the transfer resistance representing the influence of electrode reactions caused by passage of alternating current, Z_w is the Warburg impedance; the resistance R_1 and capacity C_1 represent the influence of adsorbed intermediate products of the electrode processes on the phase shift between a c current and a c voltage applied to the cell. The protective Cd bridges can be represented by the resistance R_b connected in parallel to the electrolyte resistance R_e (We assume that the Cd bridges are dendrites of cadmium penetrating the separator and contacting both electrodes.)

Typical impedance plots in the complex plane are shown in Fig. 7 It can be seen that the cell impedance is not influenced by the formation of the Cd bridges. Hence, it seems that the contact between the dendrites of cadmium and the active mass is not ohmic, but rather it has the character of a diode In accord with some published data [3, 4], however, the results of the impedance measurements can characterise the state of the cell This is also apparent from the different courses of curves 1 and 2, or 3 and 4 The difference between the real component of charged and discharged cells is greatest at low frequencies, e g , 400% at 20 Hz, whereas it is only 30% at

10 kHz The imaginary component is always capacitive in character at low frequencies, whereas it becomes inductive at 1 - 1.5 kHz for a charged cell or above 5 kHz for a discharged cell (typically at 7 - 9 kHz).

Conclusions

(i) The method of manufacture of the separator, which determines its thickness, porosity, and wettability, also has a large influence on the distribution within it of precipitated $\text{Cd}(\text{OH})_2$.

(ii) To obtain the best protective Cd bridges, it is preferable to use a thin, nonwoven fabric with a high porosity and a low content of precipitated $\text{Cd}(\text{OH})_2$.

(iii) With commercial cylindrical cells, a higher content of $\text{Cd}(\text{OH})_2$ in the separator is necessary to compensate for the less compact packing of the rolled electrode-separator system.

(iv) A large difference between the real component of the impedance of charged and discharged cells was observed, especially at low frequencies

(v) The formation of protective Cd bridges has no influence on the results of impedance measurements.

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