

PROTECTION OF SEALED Ni-Cd CELLS FROM CELL VOLTAGE REVERSAL

I. EXPERIMENTAL CONDITIONS FOR THE FORMATION OF CADMIUM BRIDGES

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Summary

A common polyamide separator, used as the electrolyte carrier in sealed Ni/Cd cells, can also function as a carrier for the Cd/Cd²⁺ system, the deposition method being the same as that in the preparation of sintered Cd electrodes. A separator thus treated is suitable for sealed Ni/Cd cells. If it is cycled at least once in an excess of alkaline electrolyte prior to sealing, and if the cell capacity is limited by the positive electrode, the explosion hazard of the sealed cell due to voltage reversal can be eliminated by a proper choice of separator and cadmium loading. Cadmium bridges formed in the separator under these conditions prevent gas formation on either electrode, their properties depending on the quality of the separator and its loading with cadmium.

Introduction

Previous work by some of the present authors [1] was concerned with the behaviour of SAFT's commercial (VRD) sealed Ni/Cd cells in which deep discharge caused reversal of the cell voltage. Under these conditions, as expected, some of the cells showed a rapid increase in terminal voltage (to about -1.7 V) and in internal pressure. The terminal voltage of the other cells approached a value of about -0.3 V, which remained constant even during long-term discharge. At zero current, the terminal voltage rapidly returned to a constant value of 0.0 V. On charging (10 h rate, *i.e.*, 400 mA), the terminal voltage usually reached the normal value of about 1.3 V after several minutes.

Analysis of a dismantled, sealed cell, led us to assume that the described behaviour could be attributed to cadmium impurities in the separator [1],

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this is in accord with data in the literature [2] We therefore constructed a vented Ni/Cd cell with excess electrolyte and a Cd(OH)₂-loaded separator. Using this the formation of Cd bridges during deep discharge was confirmed, provided that the cell was positive limited After voltage reversal, the positive electrode soon reached the hydrogen evolution potential (about -1.1 V vs Hg/HgO) and cadmium dendrites began to grow on its surface until they reached the surface of the negative cadmium electrode The potential of the latter had to be sufficiently negative (about -0.85 V) to prevent reoxidation of the cadmium dendrites The formation of these cadmium dendrites in sealed Ni/Cd cells, and their utilization to prevent explosion by voltage reversal during excessive discharge forms the subject of the present work

Experimental

Preliminary measurements showed that pocket-type electrodes were unsuitable for this study, and therefore sintered electrodes, as used in sealed, D-size Ni/Cd cells with coiled electrodes, were used Rectangles (4 × 7.5 cm) were assembled in cells with two negative and one central positive electrode The separator was polyamide (0.12 mm, 56 g/m²) non-woven (Viledon) or (0.25 mm, 138 g/m²) woven (GLZ) fabric The true density of both separator materials was 1.16 g/cm³. The pore volumes (porosities) were calculated from these data as 1.288 cm³/g or 60% for the Viledon, and 0.950 cm³/g or 52.4% for the GLZ separator. Impregnation of the separators with Cd(OH)₂ was carried out by wetting with a CdSO₄ solution, removing the excess liquid, and repeatedly dipping in a fresh (1.3 g/cm³) KOH solution. The cadmium content in the separator was determined polarographically and expressed in mg of Cd per test cell separator The electrodes were placed in the test cell and slightly compressed by means of poly(vinylchloride) (PVC) spacers inserted between the electrode stack and the wall of the steel casing. A small Hg/HgO reference electrode (a pressed mixture of HgO and graphite in a fine nickel gauze wrapped in a polyamide separator and partly reduced to Hg) was placed close to the stack. The electrolyte was KOH of density 1.3 g/cm³

Since optimum conditions for the formation of cadmium bridges were obtained after at least one charge-discharge cycle in excess electrolyte (see Results and Discussion), the cells were subjected to at least one charge (15 h at 70 mA)-discharge (200 mA) cycle to a positive electrode cut-off potential, $E_{Ni} = 0$ V (vs Hg/HgO), in an excess of the electrolyte whenever a new separator was used. The discharge capacity thus found was mostly in the range 0.75 - 0.80 A h. The deep discharge was completed with the same current without interruption to cause reversal of the cell voltage. The formation of the cadmium bridges was determined from the terminal voltage and the potential of the nickel oxide electrode

After formation of the Cd bridges the excess free electrolyte was expelled by means of compressed air and the cell with the reference electrode was hermetically sealed with a plastic lid provided with two current

leads and three leads for potential measurements. The test cell was connected to a manometer (0 - 400 kPa) and placed in an oil bath at 25 °C. It was charged at 70 mA for 15 h and discharged at 200 mA to the cut-off potential, $E_{Ni} = 0$ V. The measured capacity was, typically, 0.60 - 0.65 A h. The deep discharge with cell voltage reversal occurred as described above, and the presence of the Cd bridges was detected in the same way as with the cells having excess electrolyte; the overpressure in the sealed cell served as an additional variable to indicate their formation.

The resistance of the cadmium bridges towards anodic oxidation was tested as follows. First, the bridges were prepared in a controlled way; the nickel oxide electrode was deeply discharged to $E_{Ni} = -0.90$ V and then loaded with a cathodic current of 50 mA for 1600 s; hence, the additional charge passed was 22.2 mA h. Afterwards, the current was reversed and the time (t_a) taken to read $E_{Ni} = -0.80$ V was determined, indicating interruption of the Cd bridges. Every selected test cell was subjected to at least ten such cathodic-anodic cycles.

Results and discussion

The change of potential with time of both electrodes of a sealed test cell discharged with a current of 200 mA (after the preparatory cycle) is shown in Fig. 1. A single layer of Viledon separator containing 170 mg of Cd was used. It is seen that the discharge capacity is limited by the positive electrode, a

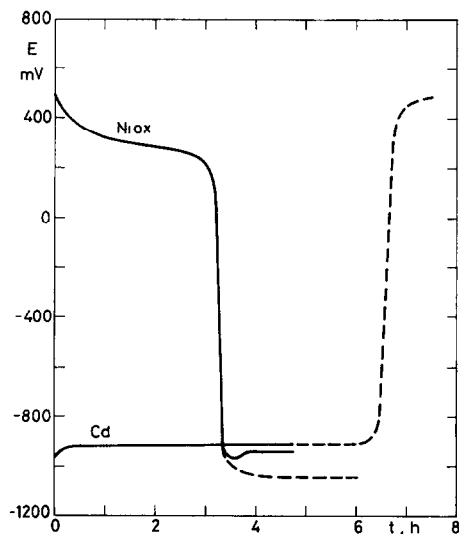


Fig. 1. Electrode potentials vs. time for a sealed Ni-Cd cell discharged galvanostatically at 200 mA (against Hg/HgO electrode). —, single layer of Viledon separator with 170 mg Cd loading, - - - -, 0 mg Cd loading.

necessary condition for the functioning of the Cd bridges [1] In the absence of the Cd bridges the potential of this electrode falls rapidly to values more negative than -1.0 V, corresponding to the evolution of hydrogen, soon after it becomes discharged When the Cd bridges are formed, however, the potential of the positive electrode passes through a minimum and returns to approach the potential of the Cd electrode, so that the negative terminal voltage of the test cell is rather low ($20 - 30$ mV), resulting from an ohmic potential drop. The potential change of the cadmium electrode is normal after a moderate decrease it becomes almost constant at about -0.85 V Prior to the formation of the Cd bridges the high capacity of the Cd electrode (compared with the positive) maintains its stable potential value. When the Cd bridges are formed, the Cd electrode is in a practically currentless state, and its potential shift to more negative values is insignificant owing to its high reversibility and ohmic polarisation.

In the case where the formation of the Cd bridges does not take place, the potential of the Cd electrode is shifted abruptly to positive values as soon as the electrode is discharged (Fig 1, dotted portion of the discharge curve)

The potential change with time of the vented test cell with excess electrolyte, after voltage reversal with the formation of Cd bridges, is shown in Fig. 2 (curve 1), and without their formation, for comparison (curve 2). At the terminal voltage of curve 2 hydrogen is evolved at the nickel oxide electrode, while the discharge reaction continues at the other Curve 1 shows a low maximum, corresponding to transitory evolution of hydrogen at the nickel oxide electrode during the formation of the Cd bridges If no Cd bridges were formed (curve 2), the negative terminal voltage would rise abruptly after about 5.5 h discharge to about -1.7 V, corresponding to the evolution of hydrogen at the nickel oxide electrode and oxygen at the other electrode

As mentioned in the Experimental section, if a test cell with a new separator is not subjected to at least one charge-discharge cycle in excess electrolyte, then the same cell under sealed conditions (without excess electrolyte) is unable to develop a Cd bridge. This is apparent from Fig. 3. Curve 1 shows the voltage change with time during deep overdischarge of a sealed test cell with two Viledon separator layers containing, in total, 1164 mg of Cd and which had not previously been cycled. Since no Cd bridge was formed, the cell was opened and subjected to one cycle in excess electrolyte, including deep discharge (curve 2). Afterwards it was sealed and subjected to another cycle with a deep discharge (curve 3) It can be seen that when Cd bridges are formed the terminal voltages during deep discharge for both vented and sealed test cells are practically the same (curves 2 and 3)

The reason why the Cd bridges can develop only after at least one charge-discharge cycle in excess electrolyte (prior to sealing the cell) probably lies in the reduction mechanism of the $\text{Cd}(\text{OH})_2$ in the separator Since direct contact between this precipitate and the negatively polarised nickel oxide electrode is not possible (particles of $\text{Cd}(\text{OH})_2$ are adsorbed in

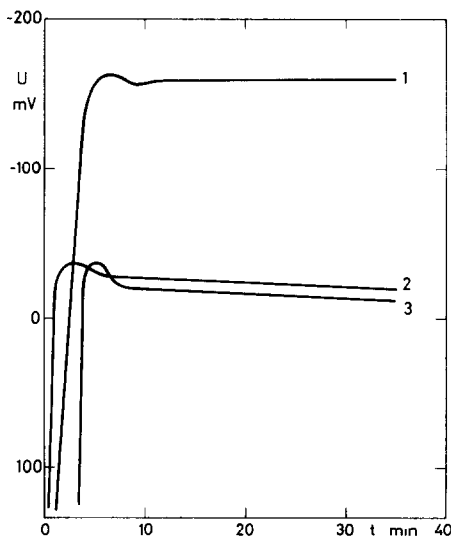
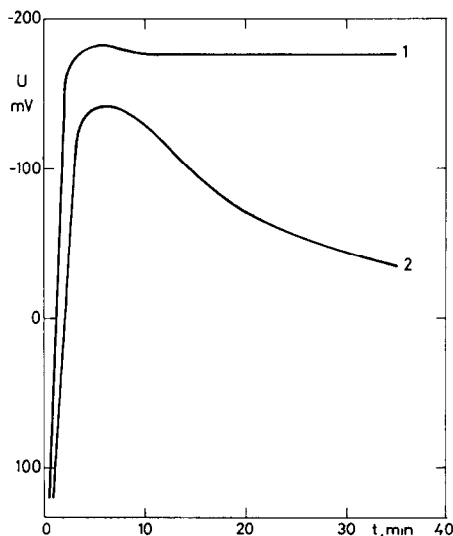
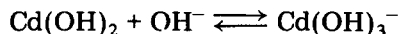


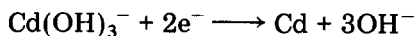
Fig 2 Terminal voltage *vs* time of a vented Ni-Cd cell during deep galvanostatic discharge at 200 mA after voltage reversal Two layers of Viledon separator containing 74 mg Cd (curve 1), and 1080 mg Cd (curve 2)

Fig 3 Terminal voltage *vs* time of Ni-Cd cells during deep galvanostatic discharge at 200 mA after voltage reversal Two layers of Viledon separator containing 1164 mg Cd Curve 1, Sealed cell which had not been precycled with excess electrolyte Curve 2, Vented cell with excess electrolyte, Curve 3, cell of curve 2 after sealing

the pores of the separator), its reduction must proceed *via* solution. A soluble hydroxo complex is formed in the excess electrolyte [3].



We assume that this hydroxo complex is reduced in contact with the nickel support



The reduction occurs as the $\text{Cd}(\text{OH})_3^-$ diffuses towards the nickel electrode. Cadmium is deposited, probably in the form of dendrites which grow and penetrate into the separator pores until some of them touch the cadmium electrode causing short circuit.

During the overdischarge period, the internal pressure of the sealed test cell was measured and the electrode potentials and pressure are shown as a function of time in Fig. 4 for 3 types of cell. Figure 4(a) refers to a cell unprotected by cadmium bridges against voltage reversal; Fig 4(b) concerns a cell protected to some extent by "weak" Cd bridges, and in Fig 4(c) the characteristics of a cell with "strong" Cd bridges are shown.

The unprotected cell showed a shift of the nickel oxide electrode potential to more negative values than -1.0 V (Fig 4(a)) accompanied by

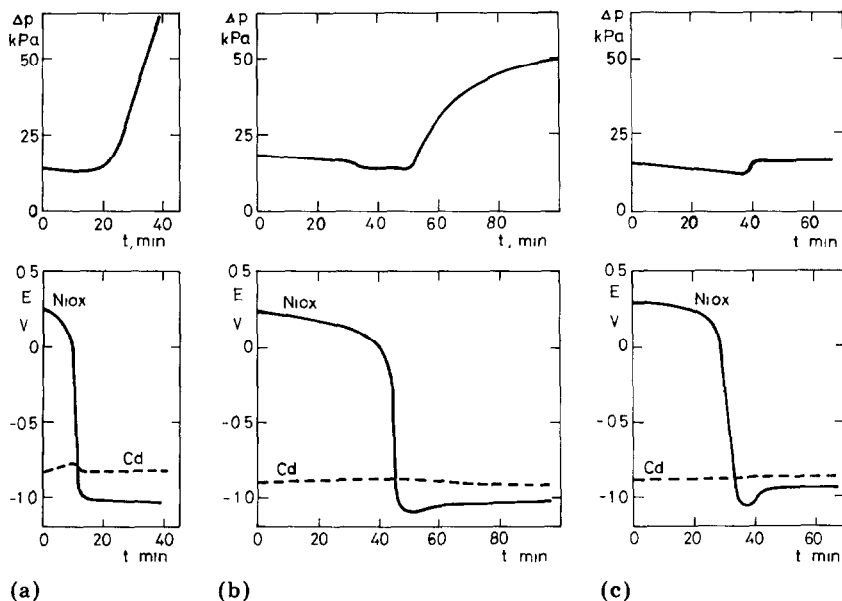


Fig 4 Overpressure and electrode potentials (*vs* Hg/HgO) *vs* time of sealed Ni-Cd cells during deep galvanostatic discharge after voltage reversal (a) Without Cd bridges, (b) with "weak" Cd bridges, (c) with "strong" Cd bridges

the evolution of hydrogen, resulting in a linear increase in the pressure with a slope proportional to the current load

In the presence of "weak" Cd bridges (Fig 4(b)), the nickel oxide electrode potential is shifted to reach a minimum below -1.0 V and then returns to approximately -1.0 V. The pressure increase is initially linear, but it then slows down until the pressure reaches a steady value, suggesting that protective Cd bridges were formed after the voltage reversal, and their strength increased gradually to cause short circuit of the electrodes

When the Cd bridges formed immediately or soon after the potential of the nickel oxide electrode had dropped below -1.0 V (Fig 4(c)), the potential minimum was more pronounced, since it rapidly increased to -0.9 V, and the pressure increase was difficult to measure, the evolution of hydrogen at the nickel oxide electrode being negligible

The physical structure of the separator influences the formation of Cd bridges as shown in Fig 5. The thinner, more porous, Viledon nonwoven separator is preferable since it obviously causes less hindrance to the growth of the cadmium dendrites. The effect of the separator thickness on performance can be seen from Fig 6. In a vented cell with excess electrolyte, one layer of the Viledon separator (containing 20 mg of Cd) allows the formation of Cd bridges, whereas two layers (containing 20 mg of Cd each) prevent it. The interelectrode distance is too large in the latter case and a higher Cd loading would be necessary for the bridges to form

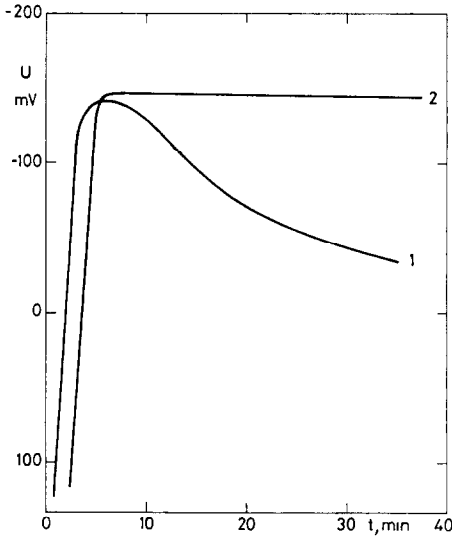


Fig 5 Terminal voltage *vs* time of vented Ni-Cd cells during deep galvanostatic discharge after voltage reversal 1, Two layers of Viledon separator containing 1080 mg Cd, 2, two layers of GLZ separator containing 904 mg Cd

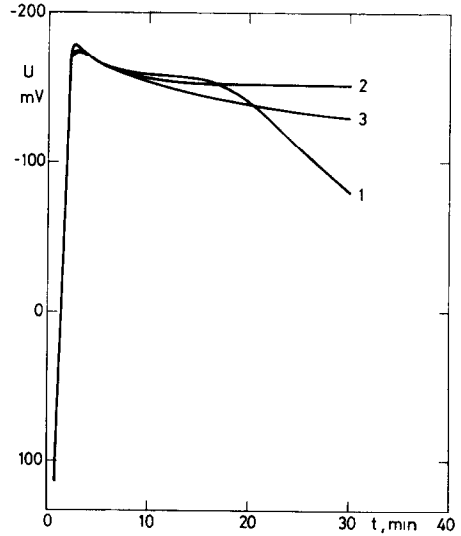


Fig 6 Terminal voltage *vs* time of vented Ni-Cd cells during deep galvanostatic discharge after voltage reversal 1, One layer of Viledon separator containing 20 mg Cd, 2, two layers, 40 mg Cd, 3, three layers, 60 mg Cd

TABLE 1

Discharge capacities (*C*) and self-discharge after 120 h of Ni-Cd test cells with different Cd loading

Cell no	Cd loading (mg)	<i>C</i> (mA h)	Cd bridge	Self-discharge (%)
1	582.0	590	yes	68.00
2	86.4	664	yes	20.50
3	32.4	601	yes	18.85
4	19.5	710	yes	18.87
5	13.2	730	yes	16.40
6	20.4	698	yes	11.75
7	11.0	620	yes	22.25
8	0	636	no	14.80
9	0	684	no	23.70

With a higher Cd loading, however, a more rapid self-discharge may be expected. To examine this we used a test cell with one layer of Viledon separator. The results are given in Table 1. Excluding the last two cases of zero Cd loading, the Cd bridges functioned reliably. Self-discharge varied between 12 and 24% over 5 days, except for the highest Cd loading (582 mg Cd; 68%), and is, therefore, comparable with non-loaded cells. It seems therefore

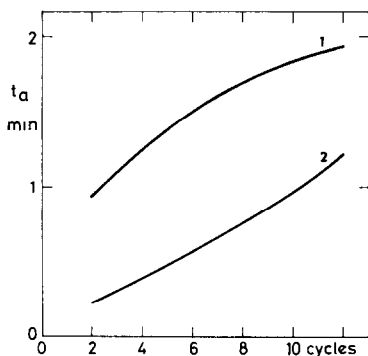


Fig 7 Strength of Cd bridges vs number of cycles of sealed Ni-Cd cells. One layer of Viledon separator 1, 173 mg Cd, 2, 65 mg Cd

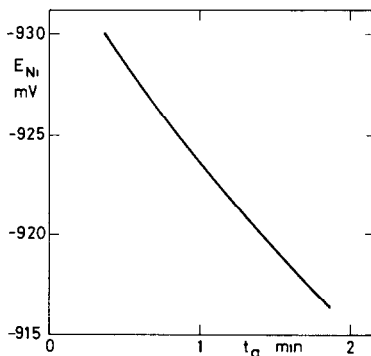


Fig 8 Potential of the nickel oxide electrode vs the time taken for the Cd bridges to break down (*i.e.*, their "strength") of a sealed Ni-Cd cell (*vs* Hg/HgO). One layer of Viledon separator, 173 mg Cd

that, except when the loadings are very high, the cadmium present in the separator does not always cause a more rapid self-discharge

To characterise the strength of the Cd bridges, we measured the time necessary for their disruption by anodic oxidation. The results for two typical sealed test cells, each containing one Viledon layer with Cd loadings of 65 and 173 mg, respectively, are shown in Fig 7. In both cases the strength of the Cd bridges increased with the number of cathodic-anodic cycles. Also, as expected, stronger Cd bridges were formed in the test cell with the higher Cd loading.

To elucidate the gradual strengthening of the Cd bridges, we measured the nickel oxide electrode potential, E_{Ni} , at the end of discharge, *i.e.*, after the controlled formation of Cd bridges had finished. It is seen from Fig 8 that as the strength of the Cd bridges ($\equiv t_a$) increased, E_{Ni} decreased. It may be assumed that this potential shift is caused by the Cd bridges increasing both in number and in thickness.

Conclusion

At least one charge-discharge cycle in excess electrolyte prior to sealing is necessary to form protective Cd bridges in sealed Ni/Cd cells. Thinner, and more porous separators containing adsorbed $Cd(OH)_2$ give stronger and more reliable Cd bridges. Two separator layers require a substantially higher $Cd(OH)_2$ loading than one layer. The strength of the Cd bridges, characterised by the time necessary for their disruption by anodic corrosion, increases with the number of cathodic-anodic cycles carried out with the nickel oxide electrode. The self-discharge of sealed Ni/Cd cells is independent of the $Cd(OH)_2$ content in the separator over a wide range of loadings. Further, the protection of cells by the use of cadmium bridges has

the advantage that it offers protection when the cells are sealed. This is not the case for antipolar mass cells which are also not completely protected against the consequences of cell reversal; the start of hydrogen evolution is merely delayed.

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