

Aspects of nickel-cadmium cells in single cycle applications.

III. Effects of electrolyte additives on cadmium hydroxide crystal growth in sintered nickel negative electrodes during discharged storage

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The single duty cycle application requires nickel-cadmium cells to be stored for long periods in a discharged, short-circuited state. Under these conditions $\text{Cd}(\text{OH})_2$ active material in the negative electrode is subject to crystal growth processes which result in reduced charge efficiency when cycled after storage. Of equal importance, however, is the observed gross redistribution of $\text{Cd}(\text{OH})_2$ active material, whereby crystals penetrate into the separator, sometimes as far as the positive electrode. This must be considered undesirable and could lead to internal short-circuiting of the cell. This paper examines the effects of various surfactant electrolyte additives on $\text{Cd}(\text{OH})_2$ crystal growth and capacity of sintered, negative electrode material, stored in excess 6 M KOH, at various temperatures between + 30 and + 60° C. Results show that, under the test conditions, low concentrations ($\leq 0.1\%$) of the anionic surfactants sodium lauryl sulphate and turkey red oil strongly suppress $\text{Cd}(\text{OH})_2$ growth and result in markedly higher aged electrode capacities compared to control electrodes stored in the absence of these additives.

1. Introduction

There is an interest in the use of sealed, secondary nickel-cadmium cells as reserve systems which may be activated by an electrical input [1]. Such applications require the cell to be stored short-circuited for periods up to 10 years in ambient temperatures between - 40 and + 70° C. Activation is achieved by a single, rapid charge within 1 h at operational temperatures between - 30 and + 55° C. Activated cells are required to remain on open circuit stand, at the operational temperature, for up to 24 h and then discharge at the 24 h rate to yield energy densities of between 40-50 Wh l⁻¹, 4-6.5 Wh kg⁻¹.

Fresh nickel-cadmium cells can meet these targets except at the very lowest temperature (- 30° C) where the volumetric energy density becomes marginal [2]. Stored cells, however, undergo a reduction in their ability to accept charge and the volumetric energy density may decrease to values below the target over the complete operational temperature range [1, 2].

Active materials in both positive and negative plates of nickel-cadmium cells, undergo modifications during storage in the discharged state which result in reduced charge acceptance of the electrodes. These losses in charging efficiency have been interpreted in terms of crystallographic re-arrangement of $\text{Ni}(\text{OH})_2$ at the positive electrode

[3–5] and crystal growth of $\text{Cd}(\text{OH})_2$ at the negative electrode [3].

Capacities of sealed nickel–cadmium cells are normally limited by the positive electrode and, therefore, any reductions in charge acceptance of stored cells should reflect the ageing process at this electrode. Bramham *et al.* [3] have shown this to be true with nickel–cadmium button cells stored discharged (but not short-circuited) for periods of up to 5 years at $+20^\circ\text{C}$; capacities of positive electrodes taken from these cells were less than those of corresponding negative electrodes during the first cycle, measured under a variety of charge/discharge conditions, namely temperatures of $+20$ and -20°C , rates of 1 and 10 C and charge inputs of 50% and 200% of rated capacity. Charging efficiency losses at negative electrodes were mainly associated with full charging, which does not usually occur in sealed cells due to the excess $\text{Cd}(\text{OH})_2$ ‘charge reserve’. This picture has been confirmed by our own studies with sintered plaque electrodes taken from sealed, cylindrical cells, stored in the short-circuited condition, at temperatures between $+20$ and $+50^\circ\text{C}$, for up to 1 year; for the first cycle following storage, using a regime of 1.2 C charge for 1 h, then 0.2 C discharge, at $+20^\circ\text{C}$, all negative electrode capacities were significantly greater than those of the positive electrode. These tests are continuing for longer storage periods and it is possible that cells may eventually become ‘negative limited’, particularly at the higher storage temperatures. Bramham *et al.* achieved such a condition with a button cell stored for 1500 h at $+70^\circ\text{C}$, then cycled at $+20^\circ\text{C}$ on a regime of 1 C, 200% input charge and 1 C discharge [3]. At operational temperatures of -30°C or below, even fresh cell capacities may become dependent on the negative electrode charge acceptance [2].

Even if a cell remains positive-limited, the crystal growth at the negative, consisting of large hexagonal plates of $\text{Cd}(\text{OH})_2$ which penetrate into the separator [1, 3] (see Figs. 2 to 4), raises the question of possible internal short-circuiting of the cell electrodes. Similar $\text{Cd}(\text{OH})_2$ crystal growths have been observed at negative plates during cell cycling [6, 7] and these have been shown to extend on to the positive electrode [7]. Barnard *et al.* [6] claimed that such material consisted principally of a non-conducting, electrochemi-

cally inactive form of $\text{Cd}(\text{OH})_2$. Dick *et al.* [7] interpreted their results in terms of ‘soft short’ formation in which interelectrode $\text{Cd}(\text{OH})_2$ is converted to cadmium metal only towards the end of charge, and rapidly discharges on open circuit stand. Nevertheless, the possibility of internal electrode shorting during long-term short-circuit storage cannot be completely ruled out and such excessive redistribution of active material must, in any case, be considered highly undesirable.

Owing to the small, but finite solubility of $\text{Cd}(\text{OH})_2$ in the cell electrolyte (about $10^{-4}\text{ mol l}^{-1}$ at 25°C , in 6 M KOH [8]), the mechanism of crystal growth probably involves a dissolution/recrystallisation process. Soluble cadmium exists as anionic species such as $\text{Cd}(\text{OH})_4^{2-}$, $\text{Cd}(\text{OH})_3^-$, etc. [8] and crystal growth would involve surface adsorption of these ions, followed by migration and final incorporation into the $\text{Cd}(\text{OH})_2$ lattice at surface sites such as kinks and steps [10]. Dissolution would proceed by the reverse process. These mechanisms may be inhibited by traces of surface-active materials in the electrolyte which can compete for surface sites with the hydroxy-cadmium anions. Such additives are commonly organic molecules and in normal multicycle applications, they would be subject to oxidative degradation at the positive electrode. But in applications calling for a single duty cycle, or limited number of cycles, this will not apply. The objective of the work presented in this paper, therefore, was to examine the effects of various organic electrolyte additive compounds on the growth and capacity of $\text{Cd}(\text{OH})_2$ in sintered, negative electrodes after storage in the discharged condition. A range of surfactant molecule types were investigated. Negatively charged anions might be expected to compete most effectively with the cadmium ions at growth centres, but other materials were included for comparison having cationic, nonionic and amphoteric properties.

2. Experimental

Circular discs, 27 mm diameter, were punched from a single strip of freshly manufactured negative electrode material, supplied by Chloride Alcad Limited (Ponthenri, UK). A nickel wire connection was secured by means of a nickel-plated steel nut

Table 1. Additives used in initial exploratory work

<i>Additive</i>	<i>Surfactant class</i>	<i>Chemical composition</i>
Ethomeen C/25	Cationic	Ethoxylated fatty amine
Tetraethylammonium hydroxide	Cationic	Quaternary ammonium compound
Cetyltrimethylammonium hydroxide	Cationic	Quaternary ammonium compound
Sodium lauryl sulphate	Anionic	Sodium salt of sulphated lauryl alcohol
Turkey red oil	Anionic	Sulphated castor oil (ricinoleic acid)
Miranol C2MSF	Amphoteric	Imidazoline ring with fatty acid groups
Ethylan BCP	Non-ionic	Nonyl phenol ethoxylate
Thiourea	Non-ionic	(NH ₂) ₂ CS
Diethyl thiourea	Non-ionic	(Et NH) ₂ CS
Dibutyl thiourea	Non-ionic	(BuNH) ₂ CS
Propargyl alcohol	Non-ionic	CH≡CH · CH ₂ OH
Butynediol	Non-ionic	CH ₂ OH · C≡C · CH ₂ OH
Surfynol 104	Non-ionic	2:4:7:9 tetramethyl 5-decyn 4:7 diol
Surfynol 440	Non-ionic	Ethoxylated form of Surfynol 104
Surfynol 465	Non-ionic	3½ mol ethylene oxide As surfynol 104 but with 10 mol ethylene oxide
Pepsin, carboxymethyl cellulose, dextrin, polyvinyl alcohol		Saturated polyhydroxy compounds
Caffeine		Cyclic diurea derivative
Resorcinol		Dihydric phenol

Table 2. Capacities of sintered nickel–cadmium electrodes stored for 2 months at various temperatures in excess 6 M KOH, containing anionic surfactant additives

<i>Electrolyte additive</i>	<i>Storage temperature (° C)</i>	<i>Capacity of fresh electrode (mA h)</i>	<i>Capacity of aged electrode (mA h)</i>
No additive	30	94	23
	36	100	11
	40	105	4
	50	100	4
	60	104	1
0.1% sodium lauryl sulphate	30	96	106
	36	96	90
	40	99	66
	50	100	8
	60	94	5
0.1% turkey red oil	30	93	87
	36	96	74
	40	97	67
	50	103	9
	60	94	7

and bolt, through a 3 mm diameter hole, punched into each disc. The active cross-sectional area of each disc was 565 mm² and the nominal capacity was 125 mA h.

A preliminary set of storage tests was conducted, using an arbitrarily chosen range of 21 additive compounds of varying surfactant class and chemical composition (Table 1). Certain of the compounds included were known additives for electroplating and metal treatment solutions, achieving effects such as grain refinement, levelling, brightening, inhibition of hydrogen evolution, etc.

Electrode discs, in the as-received condition, were immersed in open beakers of fresh, clean (no additives) 6 M KOH at + 20° C, with a nickel mesh counter electrode and a half-charged nickel hydroxide reference electrode fitted into a glass luggin capillary tube. Reference electrodes were calibrated against a standard dynamic hydrogen electrode [9] and agreed with each other to within a few mV. The potential difference of the cadmium/reference couple in this arrangement is close to the voltage of the actual cell.

The electrode discs were subjected to a single cycle in the test cell, consisting of 54 min constant current charge at 125 mA (90% input at the 1 C rate), followed by a 5.6 mA constant current discharge (C/24 rate) to 1 V cut-off with respect to the reference electrode. An average discharge capacity of 98 mA h, with a standard deviation of 3 mA h, was recorded under these conditions.

The discharged discs were stored in 250 ml, sealed, airtight, Pyrex glass containers, filled with 6 M KOH, containing 0.1% w/v additive, for 56 days at + 60° C ($\pm 1^\circ$ C). A disc stored in electrolyte without any additive served as a control. On completion of the storage period, the jars were cooled to room temperature and the electrodes recycled as before in clean 6 M KOH.

In these tests only the two anionic additives, turkey red oil and sodium lauryl sulphate, showed any measurable beneficial effects relative to the control electrode. Scanning electron microscope (SEM) examination and energy dispersive analysis of X-rays (EDAX) of the disc surfaces revealed that sodium lauryl sulphate in particular had caused a marked inhibition of Cd(OH)₂ crystal growth during storage (cf. Figs. 4 and 6). All other additives tested resulted in aged capacities which were either similar to, or less than, the control

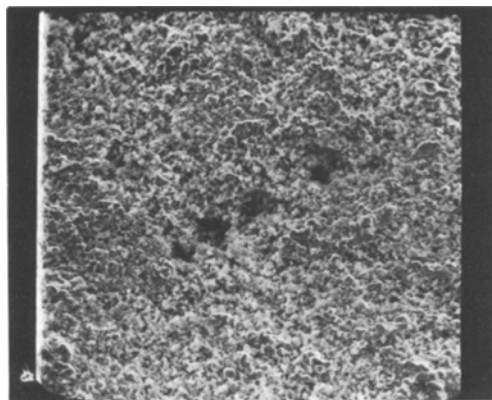


Fig. 1. Electron micrograph ($\times 600$) of a cadmium electrode in the 'as-received' condition.

electrode and produced no inhibition of Cd(OH)₂ growth as evidenced by SEM examination.

The two anionic surfactants were selected for more extensive tests in which the above experimental procedure was repeated at storage temperatures of 30, 36, 40 and 50° C ($\pm 1^\circ$ C).

3. Results and discussion

Electrode capacity measurements from the extended tests with the two anionic surfactant additives and controls are given in Table 2. Most electrodes exhibited decreased capacities when cycled after storage which was most marked at the more elevated temperatures. The increased capacity of the electrode cycled after storage in the presence of sodium lauryl sulphate at + 30° C probably originated from a 'conditioning' of

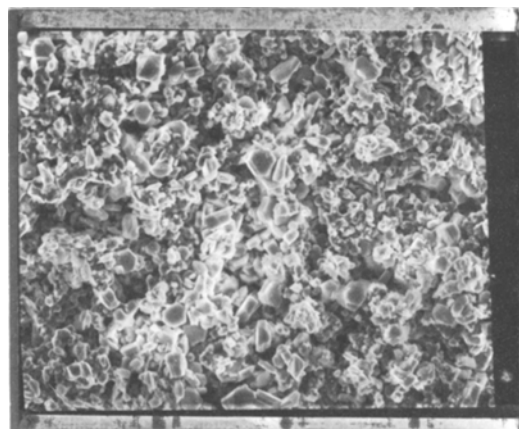


Fig. 2. Electron micrograph ($\times 600$) of a cadmium electrode stored for 56 days at + 30° C in 6 M KOH.

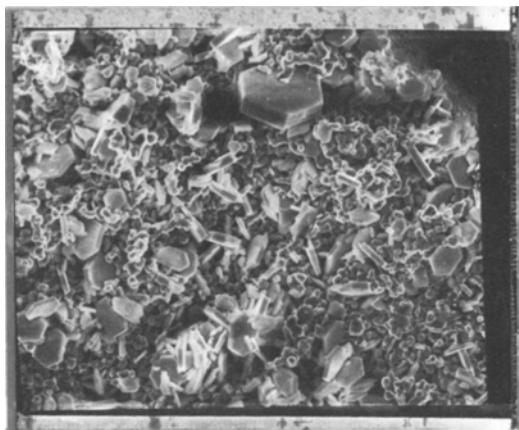


Fig. 3. Electron micrograph ($\times 600$) of a cadmium electrode stored for 56 days at $+40^\circ\text{C}$ in 6 M KOH.

active material during cycling, superimposed on a smaller storage deactivation. All electrodes stored in the presence of the anionic electrolyte additives had significantly greater 'aged' capacities than their counterparts stored without electrolyte additives.

A typical scanning electron photomicrograph of the electrode surfaces in the 'as-received' condition is shown in Fig. 1. In all cases, storage resulted in some modifications to this structure. Crystal growth on the controls was extensive and became more severe as the storage temperature increased. SEMs of the $+30$, $+40$ and $+60^\circ\text{C}$ control electrodes are shown in Figs. 2, 3 and 4 respectively. Growth on the $+36$ and $+50^\circ\text{C}$ stored controls was intermediate between those shown. In contrast electrodes stored in the

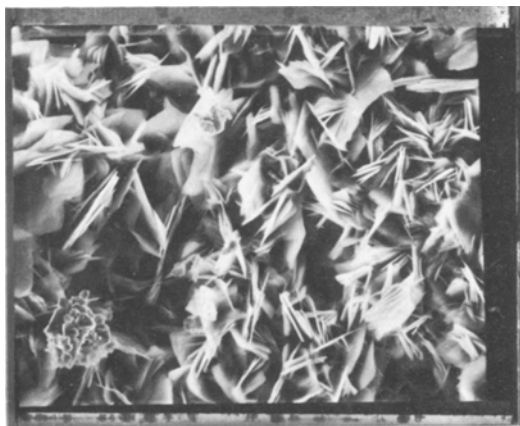


Fig. 4. Electron micrograph ($\times 600$) of a cadmium electrode stored for 56 days at $+60^\circ\text{C}$ in 6 M KOH.

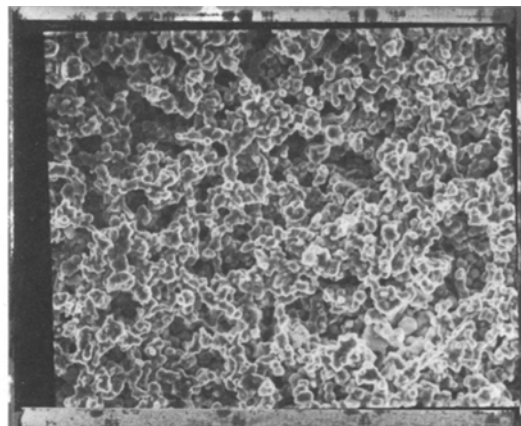


Fig. 5. Electron micrograph ($\times 600$) of a cadmium electrode stored for 56 days at $+30^\circ\text{C}$ in 6 M KOH containing 0.1% sodium lauryl sulphate.

presence of the anionic electrolyte additives underwent only small amounts of growth at storage temperatures below $+50^\circ\text{C}$. Fig. 5 shows an SEM of the disc surface stored at $+30^\circ\text{C}$ in the presence of sodium lauryl sulphate. This was typical of all discs stored with either additive at temperatures of $+30$, $+36$, and $+40^\circ\text{C}$. At $+50$ and $+60^\circ\text{C}$, in the electrolyte containing sodium lauryl sulphate, there were a number of large $\text{Cd}(\text{OH})_2$ flakes present on the discs (Fig. 6), but growth was much less in evidence than corresponding controls. The disc stored in electrolyte containing turkey red oil at $+50^\circ\text{C}$ had a similar appearance to Fig. 6, but at $+60^\circ\text{C}$ more extensive, flaky growths were observed with this additive (Fig. 7).

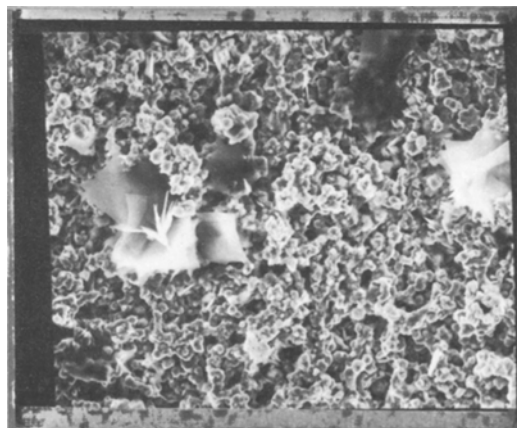


Fig. 6. Electron micrograph ($\times 600$) of a cadmium electrode stored for 56 days at $+60^\circ\text{C}$ in 6 M KOH containing 0.1% sodium lauryl sulphate.



Fig. 7. Electron micrograph ($\times 600$) of a cadmium electrode stored for 56 days at $+60^\circ\text{C}$ in 6 M KOH containing 0.1% turkey red oil.

Significant proportions of sodium lauryl sulphate remained undissolved in the electrolyte at 0.1% concentration, whereas turkey red oil was completely miscible. On an equal dissolved weight basis, therefore, sodium lauryl sulphate appeared considerably more effective in inhibiting $\text{Cd}(\text{OH})_2$ growth under the experimental conditions.

Reductions in electrode charging efficiency after storage of all control electrodes, and those stored in additive electrolytes at $+50$ and $+60^\circ\text{C}$, far exceeded any observed in sealed cell storage tests. For example, maximum recorded losses in charging efficiency in one series of cell tests, following 56 days storage, were only 50% at $+58^\circ\text{C}$ and 85% at $+70^\circ\text{C}$, with all cells remaining 'positive-limited' [1]; this compares with 99% and 95% losses with negative electrodes stored at $+60^\circ\text{C}$ in control and sodium lauryl sulphate electrolytes respectively (Table 2). The 'extra-cell' environment during storage in these tests clearly imposed a more severe set of conditions than those existing in a cell. Furthermore, the electrode deactivation in these tests cannot be explained solely in terms of $\text{Cd}(\text{OH})_2$ growth. In particular, the aged capacity of the electrode stored at $+60^\circ\text{C}$ in sodium lauryl sulphate electrolyte was only about 5% of its fresh, unstored value. However, SEM examination of this electrode (Fig. 6) indicated a very low level of $\text{Cd}(\text{OH})_2$ growth, less even than the $+30^\circ\text{C}$ stored control (Fig. 2) which had an aged capacity about 23% of its fresh value (Table 2). Thus whilst these investigations have provided a convenient comparative indication

of the electrolyte additive abilities to control $\text{Cd}(\text{OH})_2$ growth during storage, further work will be necessary to quantify the effects in the cell environment.

Conclusions

Under the test conditions, with concentrations of 0.1% turkey red oil, and even lower concentrations of sodium lauryl sulphate, in excess 6 M KOH, $\text{Cd}(\text{OH})_2$ growth in sintered nickel, negative electrode material appeared negligible after 2 months' storage at temperatures below $+50^\circ\text{C}$. Electrode charging efficiencies were hardly affected by storage at $+30^\circ\text{C}$ and were still 65 to 70% of the fresh electrode values at $+30$ and $+40^\circ\text{C}$ storage temperature. Control electrodes stored under the same conditions, in the absence of electrolyte additives, underwent more severe growth of $\text{Cd}(\text{OH})_2$ and aged capacities were between 24% and 4% of the fresh electrode values at $+30$ and $+40^\circ\text{C}$ storage temperatures, respectively.

At storage temperatures of $+50^\circ\text{C}$ and above, the presence of electrolyte additives still resulted in higher aged capacities than the controls. However, all electrode charging efficiencies declined to very low values even though $\text{Cd}(\text{OH})_2$ growth remained considerably suppressed in the presence of the electrolyte additives.

The storage conditions used had obviously caused accelerated ageing relative to the cell environment at all storage temperatures and the tests need to be repeated in actual cells. However, it is evident that low concentrations of anionic surfactants in the electrolyte of nickel-cadmium cells will significantly reduce storage effects at the negative electrode in the single duty cycle application.

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