

# *Aspects of nickel-cadmium cells in single cycle applications. I. The effects of long term storage*

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The use of sealed nickel-cadmium cells for single duty cycle applications involves certain novel features for which little or no quantitative knowledge exists. The investigations presented in this series of papers have sought answers to the questions raised in broad terms. This first paper considers the effects of long term storage (up to 10 years), in the short-circuited condition, at temperatures ranging between  $-40$ – $+70^{\circ}\text{C}$ . An accelerated test procedure was formulated to determine charge acceptance degradation of cells after storage for any given period and temperature. The results indicate that storage effects will constitute a major problem area for nickel-cadmium cells in these applications.

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## 1. Introduction

There is an interest in the use of rapid recharge secondary cells for certain new applications requiring single duty cycle. In essence, the requirement is for a primary reserve system activated by electrical input. Such applications involve a number of unusual features for secondary cells illustrated by the following specific requirements:

- (a) Single duty cycle (possible maximum of two).
- (b) Cells must be stored short-circuited for periods of up to 10 years at temperatures ranging between  $-40$ – $+70^{\circ}\text{C}$ .
- (c) Activation (charging) within 1 hour.
- (d) Energy density at the 24 hour discharge rate should be  $40$ – $50\text{ Wh l}^{-1}$ ,  $4$ – $6.5\text{ Wh kg}^{-1}$ .
- (e) Up to 24 hour open-circuit stand period following charging.
- (f) Operational temperatures (i.e. charge,

stand and discharge) range between  $-30$ – $+55^{\circ}\text{C}$ .

(g) Cells must be sealed; venting during charge is permissible provided this does not include electrolyte mist or other corrosive materials.

An overview of the secondary cell field identified nickel-cadmium as the only appropriate couple, at least in the immediate term. A literature search and consultations with manufacturers affirmed the suitability of fresh unstored commercial cells in ambient temperatures between  $0$ – $40^{\circ}\text{C}$ , but revealed some aspects for which little or no quantitative data existed and which in some instances were of a conflicting nature. The main areas of uncertainty were:

- (a) The effect of prolonged short-circuit storage on the cell charge acceptance in the first cycle and the deterioration mechanisms involved.
- (b) The problems of operating at high ( $+55^{\circ}\text{C}$ ) and low ( $-30^{\circ}\text{C}$ ) temperatures.

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(c) The effects of alternative charging methods such as pulsed and periodic reverse current (reflex charging) on the cell performance.

This paper is concerned with (a), storage effects; the other areas are considered in following publications.

The experimental work presented in this series of publications was exploratory in nature and only intended to provide a general view of what might be expected of nickel-cadmium cells for such applications. Work has now started on detailed studies of the more critical aspects identified by these initial investigations.

## 2. Storage effects

A number of degradation mechanisms are possible. Firstly, there are irreversible effects associated with the cell's passive elements such as seal integrity, separator stability, electrolyte redistribution, etc. These are important factors in all nickel-cadmium cell applications and extensive research and development work on the part of manufacturers in these areas has led to a high degree of cell reliability. It is beyond the scope of this paper to consider these features further.

Secondly, recrystallization and growth of the electrode active materials during storage results in reduced charge acceptance on the first few cycles. In extreme cases dendritic growth of the negative active material,  $\text{Cd}(\text{OH})_2$ , can cause inter-electrode shorting. However, normal nickel-cadmium cell usage involves cycled or float operations when storage deterioration is not of prime interest. Manufacturers recommend a preconditioning cycle(s) prior to use after extended storage periods. Provided no shorting has occurred, this can restore cells to near their fresh condition. For this reason storage degradation has been little studied; in particular, the effects of short-circuit storage are extremely uncertain.

Qualitatively our enquiries revealed a consensus of opinion that degradation through recrystallization and growth is confined to the cadmium hydroxide electrode. Certainly there is conclusive evidence of marked effects at this electrode. Figs. 1 and 2 show electron micrographs of aged and fresh negatives respectively; the former were taken from sintered electrode,

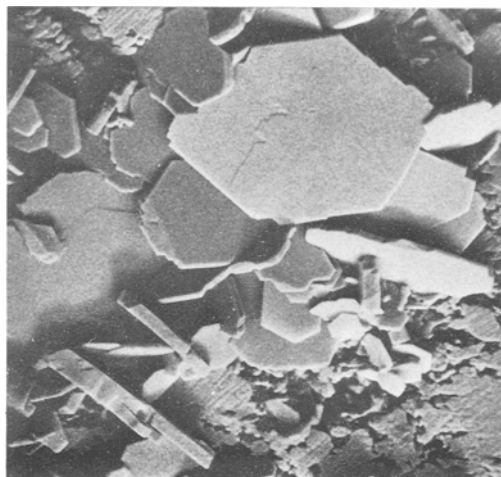


Fig. 1. Electron micrograph ( $\times 540$  magnification) of a cadmium hydroxide electrode taken from a cell after 9 years storage.

button cells provided by a manufacturer, which had been left discharged, but not shorted, for 9 years at normal ambient temperatures. No problems were thought to exist at the positive electrode, at least with short to medium term storage, although Briggs [1, 2] had reported some subtle changes in the crystallographic structure of aged  $\text{Ni}(\text{OH})_2$  electrodes. Very recently, however, work at the Royal Aircraft Establishment (Farnborough) demonstrated the considerable importance of effects at the positive electrode [3] in addition to growth of the negative active

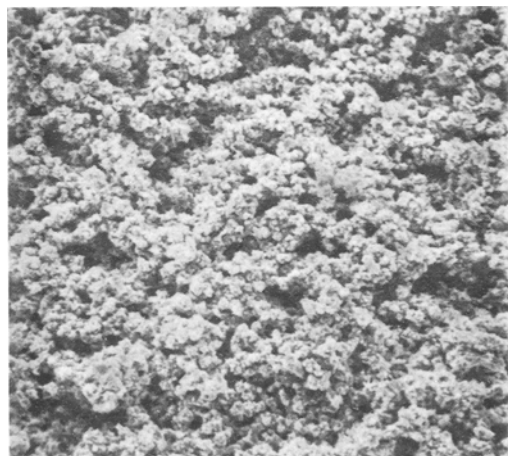


Fig. 2. Electron micrograph ( $\times 540$  magnification) of a fresh cadmium hydroxide electrode.

material. Our tests on the 9 year stored button cell electrodes confirmed the R.A.E. findings; on charging at the 1 C rate, in excess of electrolyte at + 20° C, the positives evolved oxygen within a few minutes with no accompanying hydrogen evolution at the negatives.

The R.A.E. results are of undoubted value but many questions remain concerning the storage problem as well as the actual mechanism of degradation, e.g. effects of different cell construction, sources of supply, electrode manufacturing variables and active material chemical composition, short-circuit storage effects, and charge rate, temperature and type (i.e. d.c., pulsed, reflex, etc.). A rigorous assessment of all these factors for a 10 year storage period is obviously a daunting task without a valid accelerated storage test. We are examining the possibility of employing an Arrhenius method to project cell charge acceptance, using data derived from short term storage tests at elevated temperatures. This is intended to validate the Arrhenius treatment for a specific set of charge-discharge conditions and for a single cell type. If successful, the method could be generally applicable to studies of storage factors.

Three basic assumptions are made:

- (a) The degradation mechanism responsible for reduced cell charge acceptance after storage is an activated process following the Arrhenius law, e.g.  $\text{Cd}(\text{OH})_2$  or  $\text{Ni}(\text{OH})_2$  recrystallization.
- (b) The degradation mechanism does not change with temperature or time. This may be checked throughout a test by suitably monitoring the Arrhenius constants (see below).
- (c) The degradation mechanism is first order. Modified equations can be used to fit conditions for other reaction orders.

The degradation in cell charge acceptance can then be represented by the equation:

$$\ln [\ln (C_0/C_t)] = \ln At - E/(RT). \quad (1)$$

$C_0$  is the capacity returned by the unstored cell (Ah)

$C_t$  is the discharge capacity returned after storage using the same charging regime as for  $C_0$  (Ah)

$A$  is a constant, the 'Arrhenius frequency factor' ( $\text{day}^{-1}$ )

$t$  is the storage time (days)

$E$  is an activation energy ( $\text{J mol}^{-1}$ )

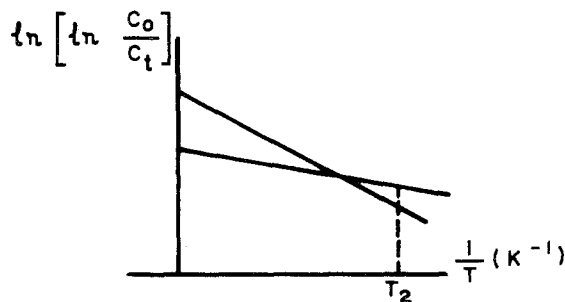


Fig. 3. Arrhenius plots of two reactions differing in their  $E$  and  $A$  values.

$R$  is the gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )

$T$  is the absolute temperature (K).

A plot of  $\ln [\ln (C_0/C_t)]$  against reciprocal temperature should be a straight line of slope  $E/R$  and  $y$ -axis intercept  $\ln At$ . Hence  $E$  and  $A$  can be evaluated for a given short time interval  $t$ , from which the cell capacity at any time and/or storage temperature can be estimated.

This technique does not consider the mechanism of degradation *per se*, but rather reflects the kinetics of the cell's capacity-limiting process. The possibility exists of a change in the predominant process at different temperatures. This will be manifested by a change in slope ( $E$ ) of the Arrhenius plot such that a higher than expected degradation will always be observed at the lower temperatures. Thus in Fig. 3 we have two superimposed reactions differing in their  $E$  and  $A$  values. The measured Arrhenius plot will then appear as shown in Fig. 4. The purpose of the initial tests reported in this paper was to establish whether or not a single predominant process was observed throughout the temperature range 20–70° C.

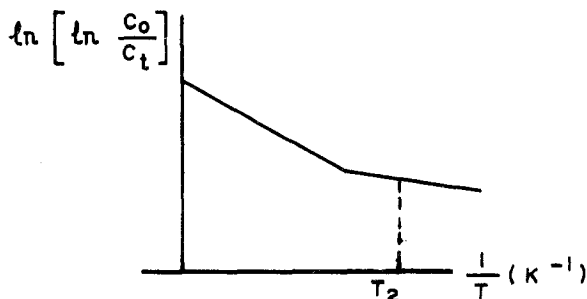


Fig. 4. Resulting Arrhenius plot on superimposing two reactions differing in their  $E$  and  $A$  values.

A further possibility is that the predominant mechanism may alter with time. This can only be established by repeating the tests at different time intervals. Such a work programme has been initiated together with a back-up programme of long term (up to 10 years) storage tests against which the Arrhenius predictions can be correlated.

Activation energies should be similar for different cells and represent the values for the degradation of the capacity-limiting process. The pre-exponential factor  $A$ , however, will tend to be specific to the type and origin (make) of the cells since it will depend in part on electrode surface areas which will vary from one cell type to another.

For this reason the extended tests now in progress encompass a range of cells of different origins. It is also intended to examine individual electrodes from these cells to assess the relative storage degradations between positive and negative electrodes.

### 3. Experimental

Twenty-five cylindrical, wound, sintered electrode cells, of nominally identical prehistory (i.e. sample from a single manufacturers' batch) and rated capacity 100 m Ah, were charged from a constant current power source in five batches of five series-connected cells. Cell temperatures were maintained at 5° C ( $\pm 2^\circ$  C), and a charging current of 100 mA (1 C) was maintained for 1.2 hours.

After charging, individual cells were discharged at an average 0.2 C rate through a 60  $\Omega$  resistor to a 1 V cut-off. Cell voltages were measured at minute intervals throughout the discharges using a Solartron digital data logger. The mean discharge current (mA) was estimated from this data and used to calculate the capacity (m Ah) to the 1 V cut-off point. This capacity was recorded as the datum ( $C_0$ ), without any further charge-discharge cycling.

Table 1. Discharge capacities of 100 m Ah cells before and after 56 days storage (mean datum capacity 84.7 mA h, standard deviation 6.77 mA h)

Cell No.	Datum capacity $C_0$ (mA h)	Capacity after storage $C_t$ (mA h)	$C_0/C_t$	Storage temperature $T$ (° C)
1	93.9	37	2.538	70
2	84.9	84.7	1.002	20
3	92.4	90.5	1.021	20
4	79.9	0	—	70
5	84.6	84.2	1.005	20
6	74.7	62	1.205	42
7	84.8	71.1	1.193	42
8	84.6	48	1.763	58
9	84.8	48	1.767	58
10	79.0	68.4	1.155	42
11	84.4	41	2.059	58
12	94.2	54	1.744	58
13	92.2	53.2	1.707	50
14	84.4	48	1.758	58
15	90.4	65.4	1.382	42
16	79.8	0	—	70
17	67.2	71.7	—	20
18	81.6	12.2	6.689	70
19	73.4	80.6	—	20
20	84.0	21.4	3.925	70
21	84.2	71.5	1.178	50
22	90.2	74.5	1.211	42
23	90.4	68.6	1.318	50
24	94.1	59.4	1.584	50
25	84.2	68.6	1.227	50

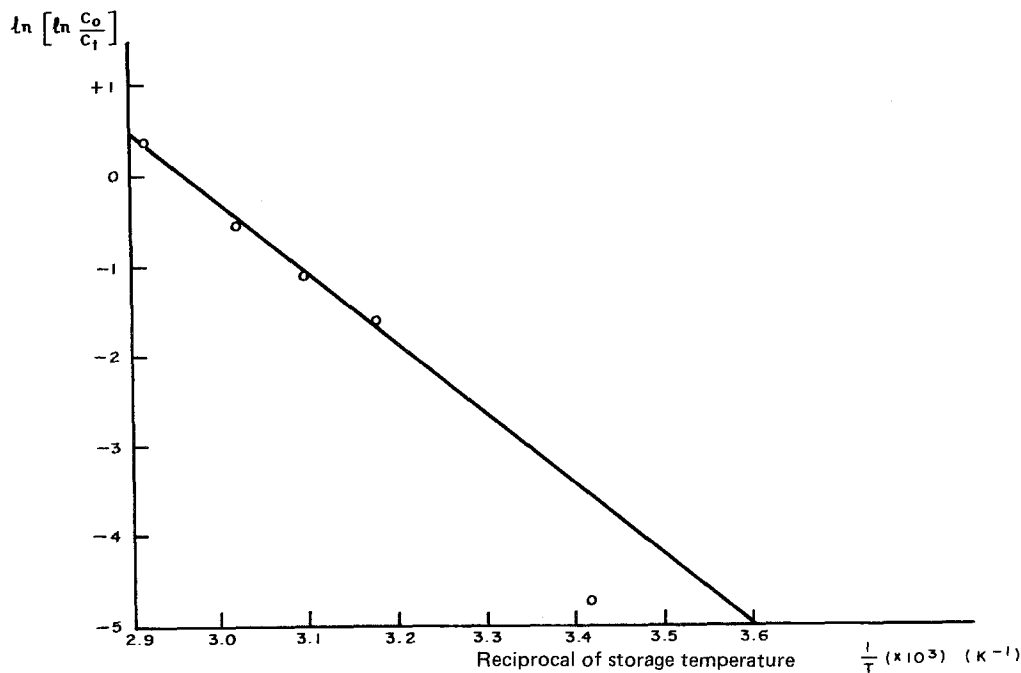


Fig. 5. Arrhenius plot for Ni-Cd cells after 56 days storage.

Short-circuit links were applied to the discharged cells which were then stored in batches of five cells at each of five different temperatures in the range 20–70°C for 56 days. Storage temperatures were controlled to  $\pm 2^\circ\text{C}$ .

On completion of the storage period the aged capacity ( $C_t$ ) of each cell was determined using exactly the same procedure outlined above for the datum capacities.

#### 4. Results and discussion

Table 1 gives the measured discharge capacities of the cells and their storage temperatures. The Arrhenius plot for this data is shown in Fig. 5. The zero values for the stored Cells 16 and 4 were not included in the analysis since the manufacturer had warned of possible short-circuiting at 70°C due to separator distortion. Equally the two results on Cells 19 and 17 at +20°C storage temperatures were excluded; both these cells had rather low datum capacities being about two standard deviations from the mean. The apparent increases in capacity after storage were therefore attributed to electrode conditioning effects masking the very small amounts of storage

deterioration at +20°C. The points for the four higher storage temperatures in Fig. 5 lay on a reasonably straight line. But the 20°C storage temperature results were considerably below this line, i.e. storage degradation was apparently much slower than expected. This is not indicative of any mechanistic changes which can only yield a higher than expected deterioration rate (see Figs. 3 and 4). The deviations from linearity were more likely caused by superimposed 'cycling-up' effects on the relatively small amounts of deterioration which had occurred under this storage condition. All cells in the extended storage test programme will be fully conditioned prior to recording the datum capacities and the longer storage periods should furnish a more accurate estimate of storage deterioration in temperatures near or below normal room temperatures.

The slope of the Arrhenius plot in Fig. 5 is numerically  $7752 \text{ K}^{-1}$ , giving a value for  $E$  of  $64.45 \text{ kJ mol}^{-1}$ . The pre-exponential factor  $A$  for our 56 day period is estimated at  $1.623 \times 10^8 \text{ day}^{-1}$ . The overall relationship is then:

$$\ln \frac{C_0}{C_t} = 1.623 \times 10^8 t e^{\left( -\frac{7752}{T} \right)} \quad (2)$$

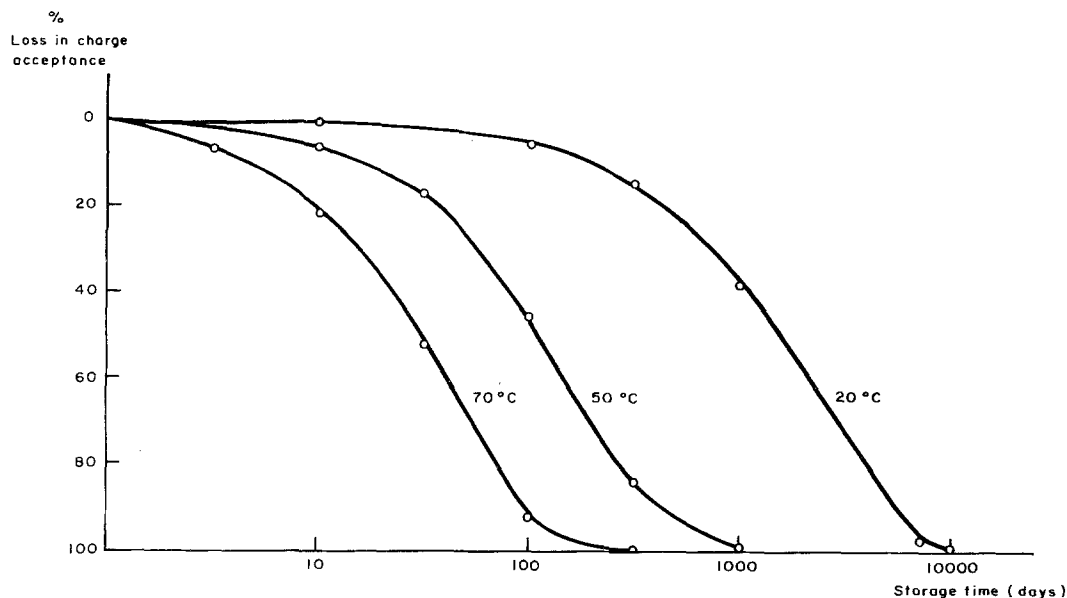


Fig. 6. Percentage loss in charge acceptance calculated from experimentally derived Arrhenius equation at various storage temperatures and times.

where  $t$  is the storage time in days and  $T$  is the storage temperature in K.

The data give a reasonable fit for a first-order reaction and therefore a cell half-life can be calculated. At a temperature of +20°C and  $(C_0/C_t) = 2$ , the time taken for decay to half the initial charge acceptance is 1320 days (3.62 years). This will apply even if the initial value had already undergone some degradation. A plot of deterioration in charge acceptance with storage time at various temperatures, calculated from the above equation, is shown in Fig. 6.

If the predictions of these storage tests are accurate the energy density of stored cells will degrade below the target (40–50 Wh l<sup>-1</sup>) within about 5½ years at +20°C, and 44 days at +70°C. More accurate predictions may be furnished by the tests now in progress, but the signs are that the problem of storage deterioration will be an acute one for this application. Some means are therefore required to either prevent degradation and/or enable cells to be reconditioned during the first charging period. The simplest method of preventing degradation would be cold storage; if this is impracticable, physical or chemical modifications may be possible to stabilize the active materials. The latter measures will require a clearer under-

standing of the degradation process, particularly at the positive electrode. Alternatively storage degradation may be cured by the use of reflex charging [4, 5], an aspect of which we are currently investigating experimentally and which will be published in a later paper.

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