

SEALED Ni-Cd CELLS: THE TEMPERATURE BEHAVIOUR OF ELECTRODES IN EXCESS OF ELECTROLYTE

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Summary

The temperature behaviour of both cadmium and nickel oxide electrodes of the sintered type (as used in sealed Ni-Cd cells) has been investigated. As a first approximation, the properties of electrodes were measured in excess of electrolyte. Measurements on various types of electrodes by several methods led to the conclusion that both capacity and service life of positive electrodes are decreased in the temperature regions above and below room temperature under the given conditions, however, there was no striking change of this kind for negative electrodes in the region of elevated temperatures. In the context of current verification of the applicability of Cd plastic bonded electrodes for sealed Ni-Cd accumulators, the temperature behaviour of these electrodes was monitored in the same experimental arrangement. A decrease in capacity was found for temperatures below room temperature. In the region of elevated temperatures, large crystals of active material are formed on the electrodes, accompanied by a decrease in the value of specific surface area. It follows from a comparison between the sintered and the plastic bonded electrodes that the latter are characterized by a higher capacity per unit volume at both room and elevated temperatures

1. Introduction

The temperature characteristics of the Ni-Cd system have been dealt with by numerous authors. *Inter alia*, hydrogen evolution was observed on negative electrodes when charging at low temperatures [1 - 13], which is due to low charge acceptance. The latter is probably caused by crystal size effects and/or the presence of γ -Cd(OH)₂ [14 - 18], as well as active mass redistribution in the bulk of the electrode [2, 7, 17, 19 - 23]. Low temperature behaviour of negative electrodes has also been studied elsewhere [24 - 26]. Certain adverse high temperature effects on these electrodes have also been described [2, 10]. Numerous papers have been devoted to the

mechanisms of both the charging and discharging reactions (solution-precipitation mechanism *vs* solid state mechanism). According to published data, the capacity of negative electrodes reaches its maximum at about +20 °C [1, 26]. Other authors measured thermal conductivities of negative electrodes [27 - 29], studied low temperature cell reversal [18], measured temperature dependences of potential together with the relevant temperature coefficients [30, 31], etc.

In the case of positive electrodes, low temperature charge acceptance and electrode resistance have been investigated [5, 6], as well as the effect of high temperatures on self-discharge rate and capacity [3, 5, 24], the effect of lithium on high temperature behaviour [10, 24], charging efficiency as dependent on temperature [5, 10, 32, 33], thermal conductivity of electrodes [28, 29], oxygen evolution as dependent on temperature [1, 10, 34, 35], and the temperature dependence of potential [30, 36 - 38]. From the viewpoint of positive electrodes, the optimum operating temperature is about +10 °C [1].

With regard to the main direction of the present work, we do not quote the numerous papers dealing with the temperature behaviour of complete cells, as this represents another major problem area.

The aim of our study was to contribute to the description and clarification of factors and mechanisms affecting the behaviour of Ni-Cd cells in regions of extreme temperature. In the present stage of our investigations, we have been engaged in a definition of the temperature dependence of some important properties of electrodes in a model experimental arrangement, major attention was paid to negative electrodes which are of essential importance from the viewpoint of long-term reliability and service life.

A further part of our extensive studies of the temperature characteristics of the Ni-Cd system was concerned with measurements of the temperature behaviour of plastic bonded electrodes (PBE). The possibilities of application of similar electrodes have been mentioned earlier [36, 39, 40]. Lately several Czechoslovak teams have been working on the production of PBE. Numerous papers have been published dealing with cadmium electrodes [41 - 52], zinc electrodes [52, 53], as well as nickel oxide electrodes [54 - 56]. In the present work, the temperature behaviour of only one type of Cd PBE was investigated. However, it is evident that, although the aspect of temperature properties is important for an actual application of PBE in sealed Ni-Cd cells, it is not the only and decisive aspect to be considered (it is also necessary to evaluate the oxygen recombination rate, the mechanical properties of electrodes, long-term reliability, and to optimize both the construction and composition of the electrodes in question).

2. Experimental

As regards the description of the experimental procedures used, we refer to our previous papers [20, 57] which contain additional detailed information.

The following types of electrodes were used for the present measurements A — negative electrodes prepared by the formate method [20], B — negative electrodes prepared by a modified formate–nitrate procedure [20], C — positive electrodes prepared by the common procedure of impregnation in a nickel nitrate melt with subsequent decomposition in a KOH solution, D — PB negative electrodes prepared from the common commercial negative material KANS (manufactured for use in pocket Cd electrodes by Lachema Bohumín, Czechoslovakia) and 10% of polytetrafluoroethylene (PTFE) by a rolling method, using a steel gauze as current collector (average thickness of the electrode 0.77 mm) Electrodes A and B were prepared so as to contain an identical amount of active material per unit volume of electrode. The construction of the model cell has been described elsewhere [20]. Counter-electrodes of the pocket type were used (negatives with a capacity of 600 mA h and positives of 750 mA h). The procedure used for measurements of capacity and service life was also the same as that described previously [20] (16 h formation at a current of 80 mA (negative electrodes) or 15 mA (positive electrodes) followed by a 60 mA discharge to 1.00 V between the measured and the counter-electrode and a 200 mA charge for 0.5 h, then automatic cycling was started: discharge at 300 mA for 9 min, 1 min pause, charge at 200 mA for 20 min, 1 min pause). The procedure used for capacity measurements (*i.e.*, in test cycles) was the same as that used during the 1st cycle

These measurements were carried out at the following temperatures —28, 0, +22, +42, and +75 °C, with an accuracy of at least ± 1 °C. After the test cycles (capacity measurements), samples were also taken for the other analyses (specific surface area, scanning electron microscopy, thermal analysis, and chemical analysis, for positive electrodes, only specific surface area measurements were undertaken) For the methods used, see our previous papers [20, 57]. Thermal analysis was carried out using the electrode material prepared in the same manner as for specific surface area measurements A Derivatograph (MOM, Budapest) was used to measure the T, TG, DTG, and DTA curves (the sample temperature, the thermogravimetric curve, its derivative, and the curve of differential thermal analysis, respectively). The samples were heated in air from 25 to 500 °C at a rate of 5 °C/min.

3. Results and discussion

3.1 Negative and positive sintered-type electrodes

The results of capacity measurements carried out during the previously-described service life test are given in Figs 1 - 3, together with the results of specific surface area measurements. It can be seen that for all temperatures studied, type B electrodes have a higher capacity than type A, this confirms the result previously obtained at room temperature [20 - 22]. Thus it is evident that in an extended temperature range also, type B electrodes are

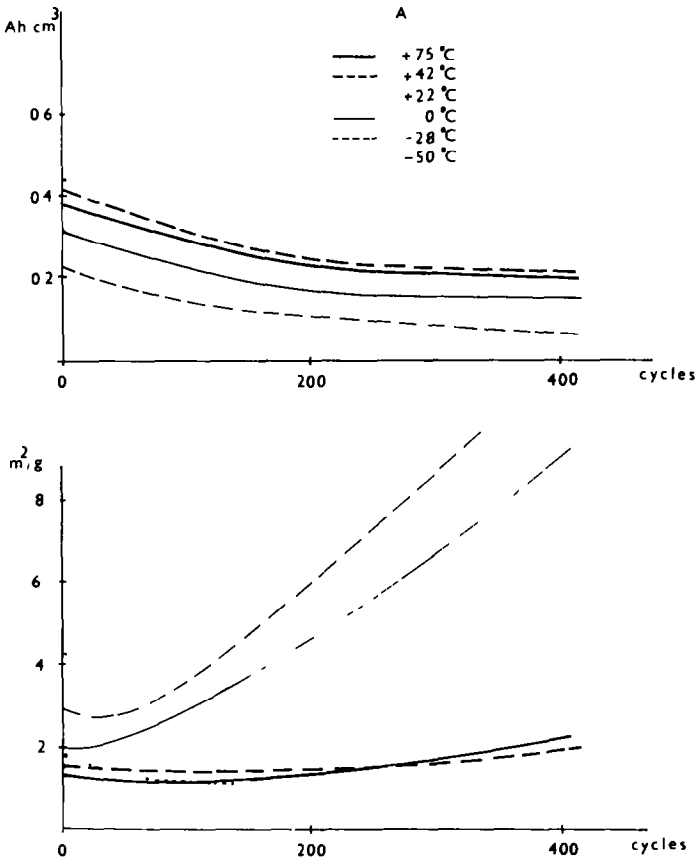


Fig 1 The average capacity per unit volume and specific surface area — electrodes A

characterized by a more advantageous service life curve. Furthermore, it follows from these results that no appreciable negative influence of elevated temperatures was found in the case of negative electrodes. However, the conditions in an actual sealed accumulator are substantially different in this respect (the effect of electrolyte carbonization). In agreement with some literature data, the capacity of electrodes decreases rapidly with decreasing temperature; this effect can be ascribed to a lower charge acceptance of the negative electrodes. The specific surface area of negative electrodes increases with decreasing cycling temperature. This is probably caused by the formation of larger crystals in the region of elevated temperatures, and/or the presence of γ -Cd(OH)₂ in the low temperature region.

For positive electrodes, optimum capacity values are reached at about +20 °C, capacity decreases with both increasing and decreasing temperature, in contrast to the results quoted for negative electrodes. This effect is probably connected with the fact that with increasing temperature, the

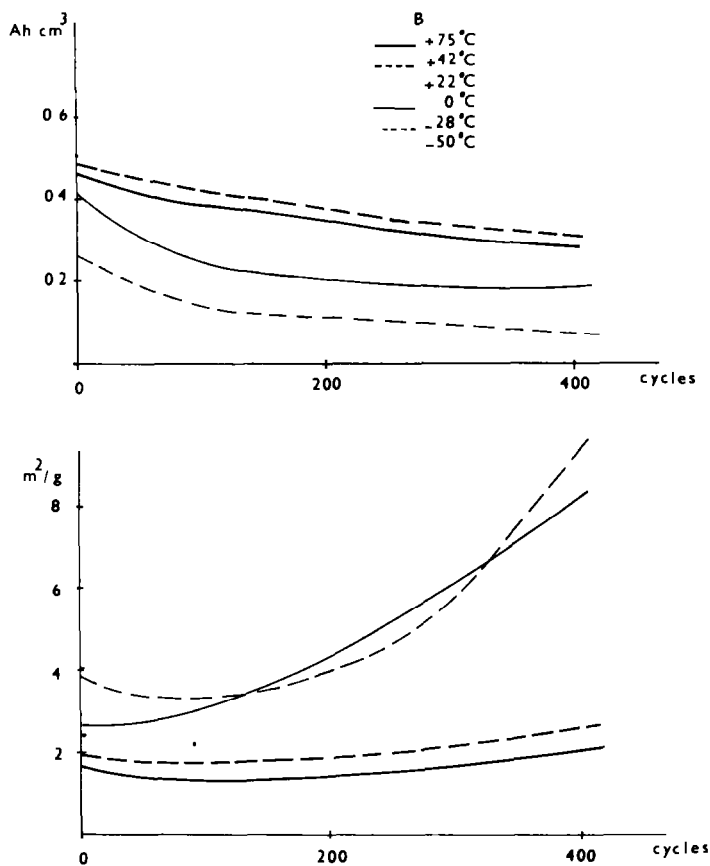


Fig 2 The average capacity per unit volume and specific surface area — electrodes B

specific surface area of the electrode material decreases in a substantial manner.

Morphological changes on the surface of negative electrodes during cycling at various temperatures were monitored using scanning electron microscopy. (Similar measurements on positive electrodes do not yield useful information; the same is also true of thermal analysis results discussed in the following paragraphs.) Figure 4 is an example of the surface of a type B electrode after 400 cycles. The results obtained may be summarized as follows: with increasing temperature, the crystal size of $\text{Cd}(\text{OH})_2$ also increases, in the case of high temperatures, relatively large crystals are found already after the initial cycles. No appreciable differences were found between electrodes A and B in this respect. Some effects which had been described earlier were again observed [20, 57], *viz.*, the crystals grow in size during cycling, some fall off, and the surface of the sintered nickel plate

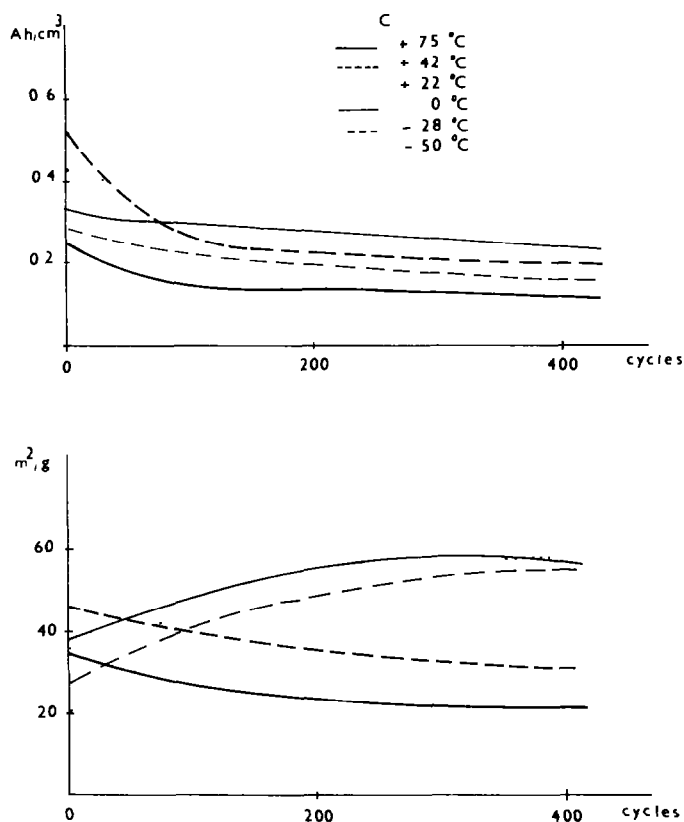
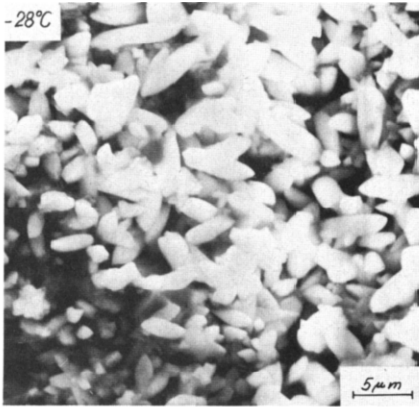


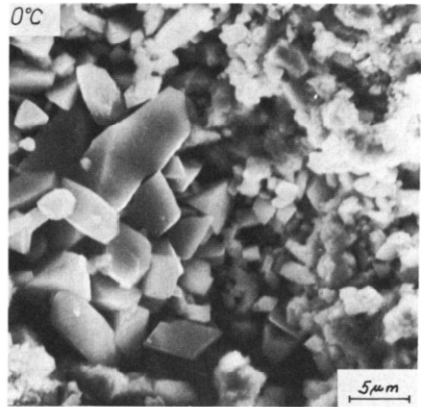
Fig 3 The average capacity per unit volume and specific surface area — electrodes C

becomes observable. Moreover, in the case of large crystals formed during cycling at elevated temperatures, a gradual (step-wise) growth of crystals is visible. It can be said that the measurements of the capacity and service life characteristics of negative electrodes, their specific surface area, and observations of the changes in their surface morphology complement one another in a satisfactory way.

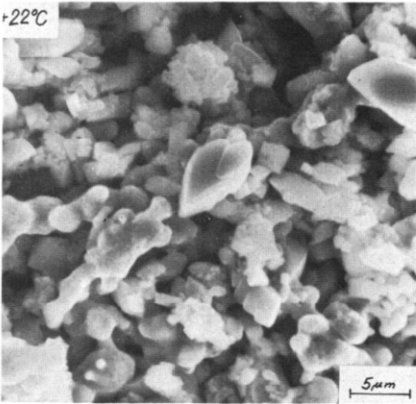
The results of measurements of the amount of Cd metal in discharged electrodes are given in Fig. 5. With increasing temperature, the amount of Cd metal in discharged electrodes increases. After the first cycle, this value is lower for type B electrodes than for type A electrodes; however, after 400 cycles this difference practically disappeared. After 400 cycles (which is the point at which the measurements were interrupted), an increased amount of Cd metal was found for all types of electrodes studied, especially in the region of elevated temperatures; the difference for low temperatures is much less pronounced.



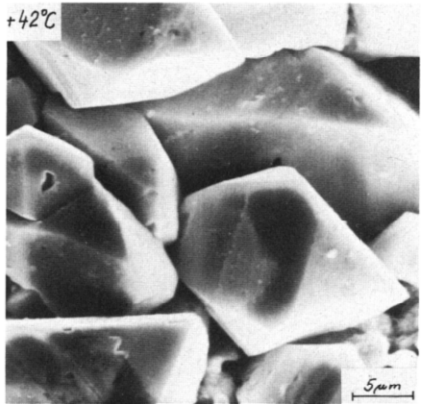
(a)



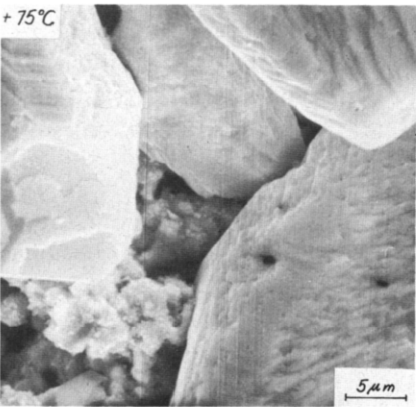
(b)



(c)



(d)



(e)

Fig 4 Surface of electrode B after 400 cycles at the given temperatures

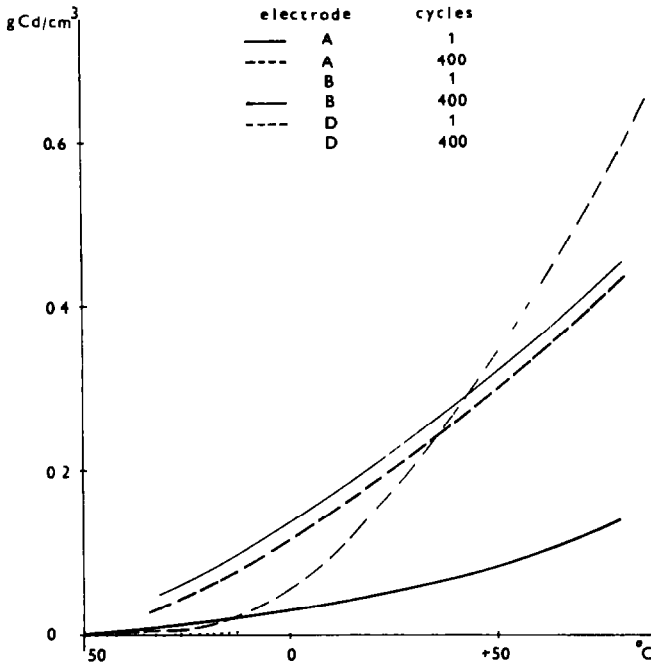


Fig 5 The Cd metal content in discharged electrodes A, B, D, cycled at various temperatures

The electrodes investigated were also subjected to thermal analysis with the objective of monitoring the relative contents of $\text{Cd}(\text{OH})_2$ and Cd in the electrode material. The mass loss corresponding to the $\text{Cd}(\text{OH})_2 \rightarrow \text{CdO}$ reaction may be evaluated relatively easily from the thermogravimetric curves. The relevant calculation leads to the $\text{Cd}(\text{OH})_2$ contents of the electrode material. The results obtained by this procedure are in qualitative agreement with the results of chemical analysis (a decrease in the contents of $\text{Cd}(\text{OH})_2$ in discharged electrodes after high temperature cycling). Unfortunately, the method does not yield sufficiently accurate data, thus making a reliable interpretation rather difficult. One of the causes of this is the fact that the amount of Cd metal cannot be read directly from the thermogravimetric curves (on the basis of the $\text{Cd} \rightarrow \text{CdO}$ reaction) because this reaction partially overlaps with the oxidation of the nickel plate.

3 2 Plastic-bonded negative electrodes

Figure 6 is a summary of the results of capacity measurements on type D electrodes during cycling, together with specific surface area measurements. It follows from a comparison of these data and those for sintered electrodes that the former are characterized by a substantially higher

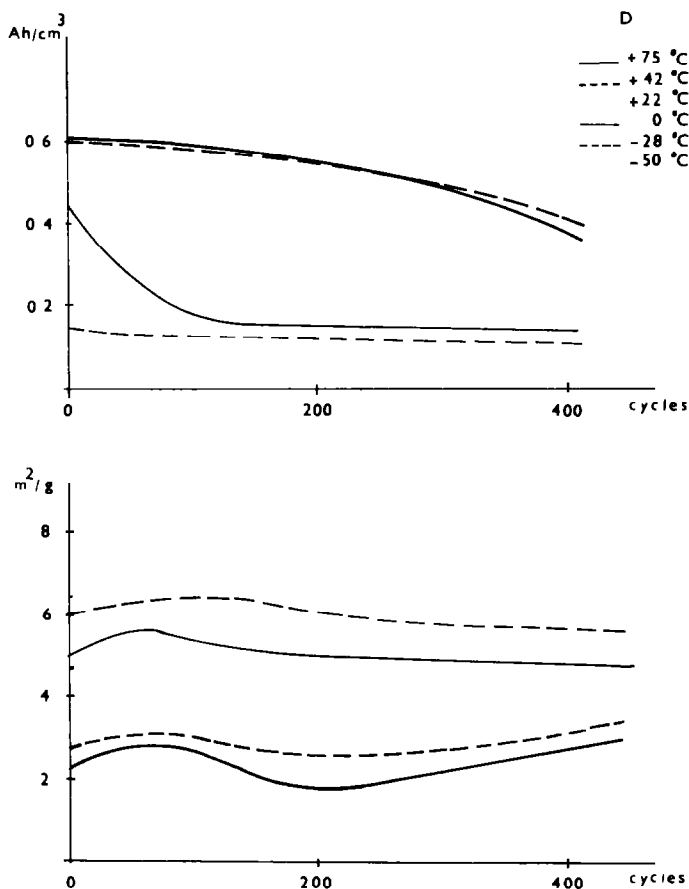
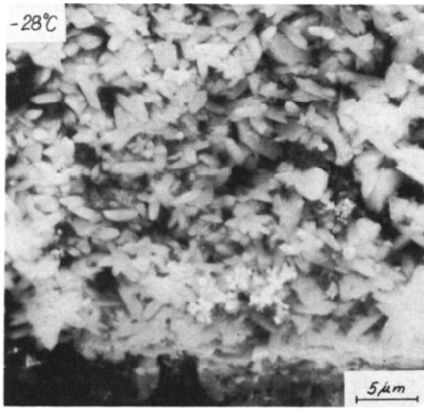


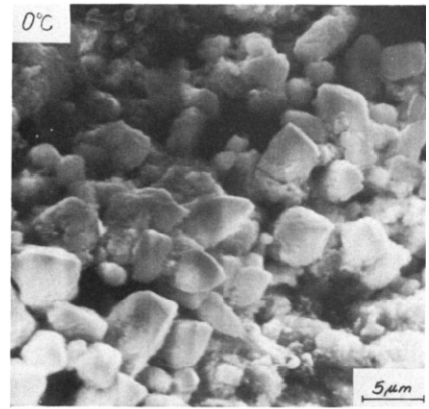
Fig 6 The average capacity per unit volume and specific surface area — electrodes D

capacity per unit volume at temperatures above +20 °C, which, however, decreases rapidly with decreasing temperature. Thus it will be necessary during the optimization of these electrodes to pay more attention to their low temperature operation. Two other effects, the same as for sintered electrodes, were observed, *viz.*, no striking decrease in capacity in the region of elevated temperatures, and an increase in the specific surface area with decreasing cycling temperature.

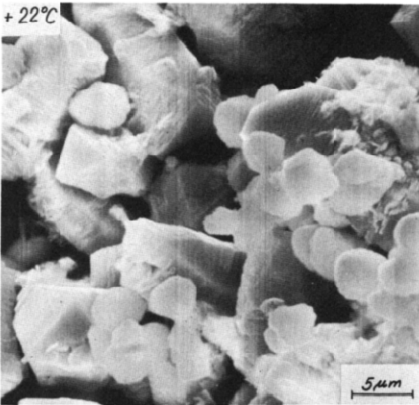
An example of surface morphology is presented in Fig. 7. During cycling, crystals of approximately the same size as for sintered electrodes are formed, and again their size increases with increasing temperature and number of cycles. Results of chemical analysis (Cd metal contents in discharged electrodes) are summarized in Fig. 5. It is clear that PBE contain higher amounts of Cd metal in the elevated temperature region than do



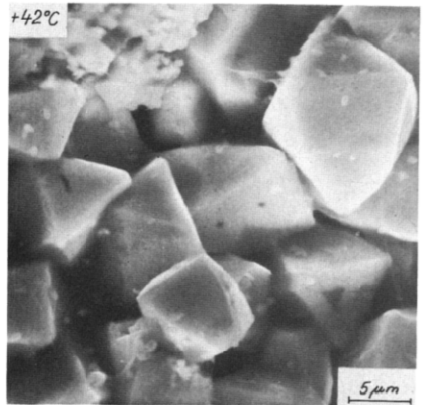
(a)



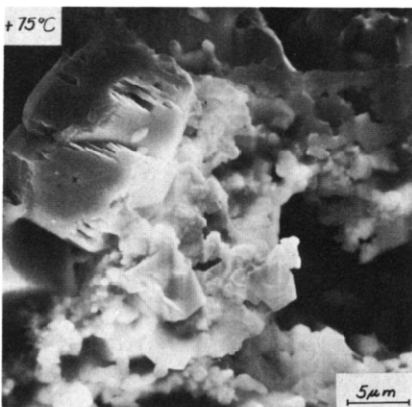
(b)



(c)



(d)



(e)

Fig 7 Surface of electrode D after 400 cycles at the given temperatures

sintered electrodes, however, their total content of active material is also higher. After cycling (especially at elevated temperatures), an increase in this content is observed.

Thermal analysis of PBE again yielded results which are in qualitative agreement with those of chemical analysis, but, of course, they cannot be used for quantitative evaluations, as discussed above. Instead of the oxidation of the sintered plate, thermal analysis curves are distorted by peaks corresponding to sintering of PTFE and its thermal decay, rendering an evaluation of the $\text{Cd} \rightarrow \text{CdO}$ oxidation impossible.

4. Conclusion

The capacity and service life characteristics of positive electrodes are decreased in the regions of both high and low temperatures. In the present model arrangement, no pronounced effect of elevated temperatures on negative electrodes was found (in contrast to lower temperatures), but under the conditions of a sealed cell, electrolyte carbonization also takes part, being caused by separator decay and accelerated by elevated temperatures. Negative electrodes prepared according to the proposed modified procedure (type B) are characterized by a more advantageous shape of the service life curve than the electrodes commonly used (type A) for all temperatures studied.

Formation of large crystals on negative electrodes was found in the elevated-temperature region, accompanied by a decrease in the value of the specific surface area. An experiment aimed at the use of thermal analysis for monitoring the Cd metal content of discharged negative electrodes did not yield satisfactory results. It was found, on the basis of chemical analysis, that the amount of Cd metal in these electrodes increases with increase in both temperature and the number of cycles

Type D Cd PB electrodes were found to be applicable in principle for use in the sealed Ni-Cd system. With regard to the fact that only the temperature behaviour of these electrodes in a model cell has been described in the present work, we are presently also investigating their recombination characteristics and other important properties. In the model cell arrangement, elevated temperatures did not result in a substantial decrease in either the capacity or the service life (in contrast to the behaviour in real sealed cells under the "starved condition"), however, in the low temperature region a rapid decrease in the electrode capacity was observed. Large crystals of active material are formed during cycling at elevated temperatures, accompanied by a decrease in specific surface area. The Cd metal content in discharged electrodes increases during cycling more rapidly than in the case of sintered-type electrodes

The investigations of the temperature behaviour of both negative and positive electrodes presented in this paper will be supplemented later by measurements of the properties of complete cells (in order to optimize their

service characteristics in the region of reduced operational behaviour) and investigations of the causes of differences in the low temperature behaviour of negative electrodes of the sintered and the plastic-bonded types

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