

## A Technical Note

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### Migration of Soluble Cadmium Species in Nickel-Cadmium Cells

R. BARNARD, G. S. EDWARDS and F. L. TYE

*Ever Ready Company (Holdings) Limited, Central Laboratories, St. Ann's Road, London N15 3TJ (Gt. Britain)*

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#### Summary

It has been shown that migration of cadmium species, in the separator region of the nickel-cadmium cell, is most likely to occur via a diffusion controlled process involving cadmate. No evidence was obtained for electrophoretic transport of negatively charged  $\text{Cd}(\text{OH})_2$  particles as recently claimed. Because the solubility of  $\text{Cd}(\text{OH})_2$  in 30% KOH is strongly temperature dependent, the migration rate similarly increases with temperature. Additions of carbonate or ammonia to the electrolyte did not significantly increase the migration rates.

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#### Introduction

It is highly desirable for nickel-cadmium cells to have good charge retention characteristics. Manufacturers are well aware of the influence of deleterious impurities such as  $\text{NO}_3^-$  which can engage in redox-shuttle reactions [1]. In addition poor charge retention can also arise from mechanical shortcircuits between the electrodes. These may function intermittently and can be due either to faulty cell assembly or degradation of the separator during elevated temperature operation. A third, and possibly the major, cause of poor charge retention or cell failure [2, 3] is the growth of cadmium dendrites from the negative plate through the separator. Dendrite growth is usually considered to proceed via soluble cadmate present in the electrolyte. However, Mayer has recently proposed [4] that negatively charged  $\text{Cd}(\text{OH})_2$  particles can be transported electrophoretically into the separator. Mayer's conclusions were based on model experiments using suspensions of  $\text{Cd}(\text{OH})_2$  in a rotating drum electrophoretic cell. Later communications [5, 6] pointed out that the results obtained by Mayer [4] are likely to be in error by several orders of magnitude. Thus the abnormally high rates of  $\text{Cd}(\text{OH})_2$  transport proposed are unlikely to be feasible. In addition to the valid criticisms expressed by James [5, 6] regarding the absolute rates of  $\text{Cd}(\text{OH})_2$  move-

ment, further difficulties arise in applying the electrophoresis model to the real battery system. First, the quantity of colloidal  $\text{Cd}(\text{OH})_2$  available from any normal sintered plate negative electrode is strictly limited, as a result of the active material being extensively agglomerated and adherent to the nickel sinter. Secondly, even assuming a low rate of electrophoretic movement is possible under strong electrolyte conditions, then, a method for its reduction to the metallic state in the separator must be found. Mayer proposes that this can occur chemically by separator degradation products. This seems distinctly unlikely because of the presence of the strongly oxidizing, higher nickel oxides in the positive electrode which would rapidly deplete soluble reducing species present in the separator. The purpose of this short communication is to provide further evidence against the electrophoretic concept and to re-emphasize the function of soluble cadmium species, particularly at elevated temperatures.

### Experimental

Cells of the type depicted in Fig. 1 were used to examine the movement of soluble cadmium species from the negative electrode through the separator

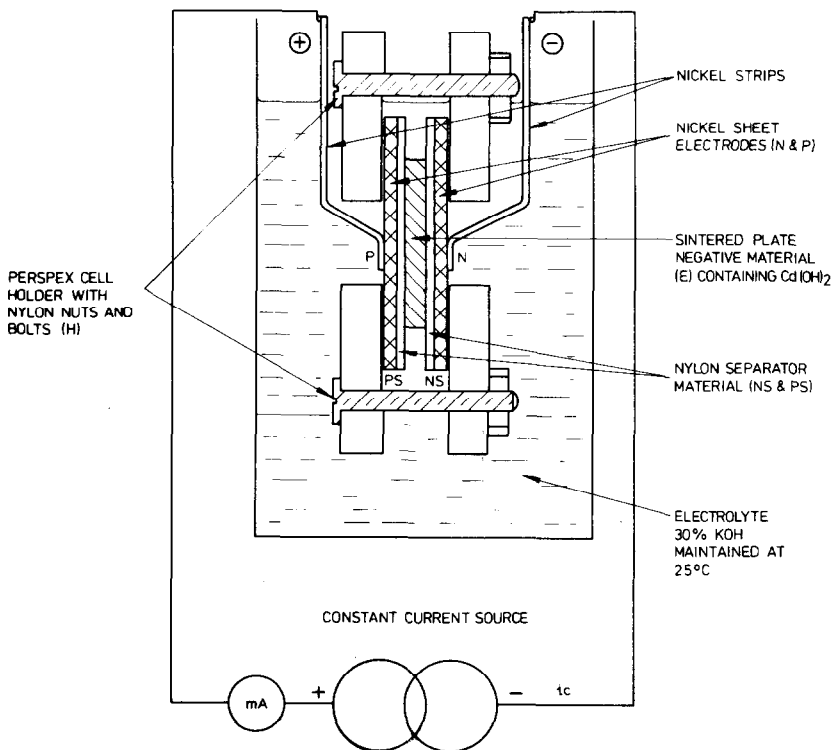


Fig. 1. Cell for electromigration experiments.

in the presence of an applied external electric field. The source of  $\text{Cd}(\text{OH})_2$  was provided by a piece of uncharged sintered plate negative electrode (E), having the dimensions  $2 \times 2.5 \times 0.065$  cm. No electrical connections were made to this "electrode". The cadmium hydroxide source was lightly clamped between two pieces of non-woven, nylon separator material NS and PS ( $5 \times 5 \times 0.038$  cm) and two identical nickel sheet electrodes ( $3.5 \times 4.5 \times \sim 0.03$  cm). The cell assembly was then immersed in electrolyte (initially pure 30% w/w KOH) contained in a polypropylene vessel with tightly fitting lid (not shown in Fig. 1). Three such electromigration cells were put together and connected in series with a constant current source supplying initially 1 mA. The cells were maintained at constant temperature in a water-bath and the current allowed to pass for 140 h. After this time the cells were disassembled and the nickel plates P and N examined visually for any deposits of Cd or  $\text{Cd}(\text{OH})_2$ . In order to follow the relative quantities of Cd deposited under different experimental conditions, the Cd levels on the positive and negative nickel plates and also in the positive and negative separator materials were determined analytically. Each cell component was immersed in excess (50 ml) 1 M HCl for 1 min to dissolve out any  $\text{Cd}(\text{OH})_2$  or Cd metal present. The solutions were analyzed for  $\text{Cd}^{2+}$  using atomic absorption spectrophotometry (Varian Techtron AA5).

## Results and discussion

The most important general observation made in every experimental run, was that a visible solid deposit was only observed on the negatively charged nickel plate. Furthermore since vigorous hydrogen evolution was observed immediately on dissolution of the grey-black deposit it was concluded that Cd metal was present.

A typical set of results at 25 °C is presented in Table 1. It is clear that the Cd present on the negative nickel plate (N) is at least 2 orders of magnitude larger than on the positive plate (P). Most, if not all, of the  $\text{Cd}^{2+}$  on

TABLE 1

Analytical data for electromigration experiments at 25 °C in 30% (7 M) KOH after 140 h

Cell component	$\text{Cd}^{2+}$ content (mg)			Average $\text{Cd}^{2+}$ content (cells 1 - 3) (mg)	Relative % $\text{Cd}^{2+}$ on each component
	Cell No. 1	Cell No. 2	Cell No. 3		
Nickel plate P	0.01	0.01	0.01	0.01	0.8
Separator PS	0.04	0.06	0.06	0.05	4.0
Separator NS	0.12	0.09	0.09	0.10	7.9
Nickel plate N	1.10	1.20	1.00	1.10	87.3

plate P arises from droplets of adherent electrolyte containing dissolved  $\text{Cd}(\text{OH})_2$ . The plates were deliberately not washed before analysis because of the possible risk of dislodging any fine loosely adherent deposits and the consequence of misleading results. The quantity of cadmium (initially as  $\text{Cd}(\text{OH})_4^{2-}$ ) present in the separator (NS) adjacent to the negatively charged nickel plate (N) is slightly larger than in the separator (PS). In both cases the levels of Cd are small reflecting the low solubility of  $\text{Cd}(\text{OH})_2$  in 30% KOH ( $1.08 \times 10^{-4} \text{ M}$  at  $25^\circ\text{C}$ ). The results show conclusively that the general direction of movement of Cd is towards the negatively charged plate. If electrophoretic transport of colloidal negatively charged  $\text{Cd}(\text{OH})_2$  particles were involved then migration towards the positively charged plate would have been expected. Clearly the experimental results obtained in this work are in direct conflict with Mayer's [4] hypothesis. Ideally for electrophoretic studies gas evolution should not occur at the current collection electrodes as this displaces the suspension. Nevertheless if electrophoretic transport was involved in the present system a significant increase of  $\text{Cd}(\text{OH})_2$  in the separator, PS would have been expected. Furthermore gas evolution would also have taken place at the stainless steel electrodes used in Mayer's experiments.

It is apparent from Table 1 that the quantity of Cd metal deposited is small (1.1 mg) in relation to the large quantity of charge passed (140 mAh). From the weight of Cd deposited an average Cd deposition current component can be estimated as  $3.8 \mu\text{A}$ . Changing the current in the range 1 - 18 mA did not alter the average weight of Cd deposited, hence it may be concluded that the system is operating under diffusion limited conditions. The majority of the current is consumed in hydrogen evolution. Because of the high concentration of supporting electrolyte the current carried by the cadmate is negligible and the cadmium species reach the nickel plate by diffusion only. A value for the diffusion limited current  $i_l$  can be calculated using the equation:

$$i_l = \frac{nFAC_b DVe^3}{\delta} \quad (1)$$

where  $n$  is the number of electrons transferred,  $F$  the Faraday constant,  $C_b$  the bulk concentration of cadmate,  $D$  the diffusion coefficient of cadmate in free electrolyte,  $Ve$  the volume fraction of electrolyte available in the separator and  $\delta$  the diffusion layer thickness. The term  $Ve^3$  in equation (1) is used as a factor to correct  $D$  to a value applicable within the separator [7, 8]. By assuming  $\delta$  to be equal to the separator thickness (0.038 cm), taking  $A$  as  $5 \text{ cm}^2$ ,  $D$  as  $5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  [9],  $C_b$  as  $1.1 \times 10^{-7} \text{ M cm}^{-3}$  and  $Ve$  as 0.8,  $i_l$  can be estimated as  $7.2 \mu\text{A}$ . This value is in reasonable agreement with that estimated analytically. It should be noted that Cd metal deposition was restricted to the nickel face closest to the  $\text{Cd}(\text{OH})_2$  source electrode and occupied a superficial area similar to the latter ( $\sim 5 \text{ cm}^2$ ). As expected, by using four layers of separator the quantity of cadmium migrating to the negative plate was reduced ( $0.64 \text{ mg Cd}^{2+}$  after 140 h at  $25^\circ\text{C}$ ).

It is claimed [2 - 4, 10] that the presence of  $\text{CO}_3^{2-}$  in the electrolyte drastically increases the migration rate of soluble cadmium species, however, this could not be confirmed in the present work (1.4 mg  $\text{Cd}^{2+}$  after 140 h at 25 °C in 30% KOH containing 20%  $\text{K}_2\text{CO}_3$ ). Similarly using 30% KOH saturated with  $\text{NH}_3$  no increase in the migration rate could be detected.

The most significant changes in migration rates were induced by changes in temperature as can be seen from Fig. 2. This is a consequence of the temperature dependence of  $\text{Cd}(\text{OH})_2$  solubility and the enhanced diffusion rates produced [3]. At this point it is worth noting that for cells/battery packs operating at ambient temperature (25 °C) the internal temperature is usually appreciably greater.

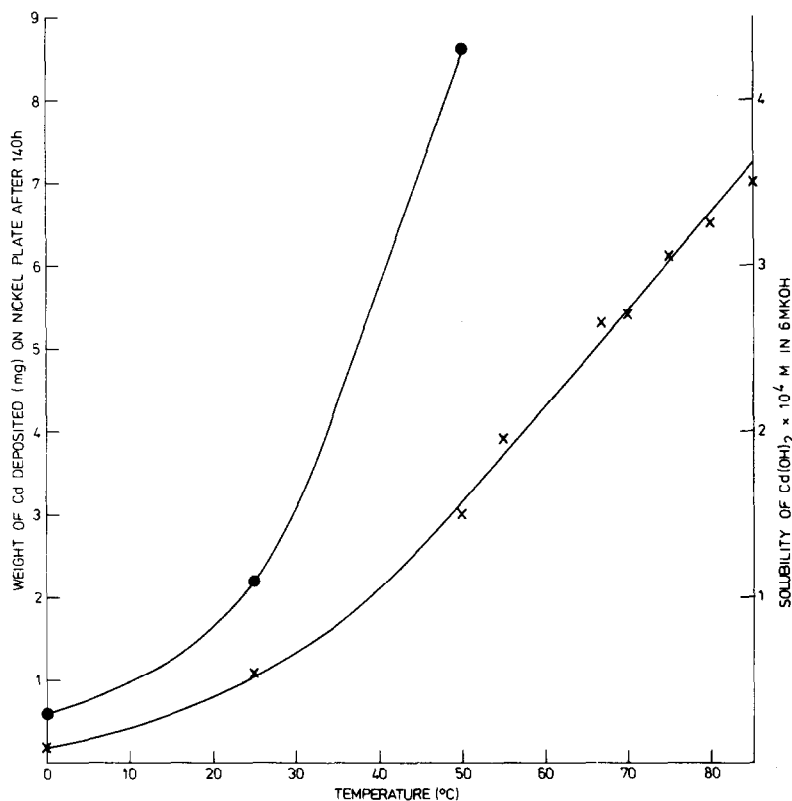
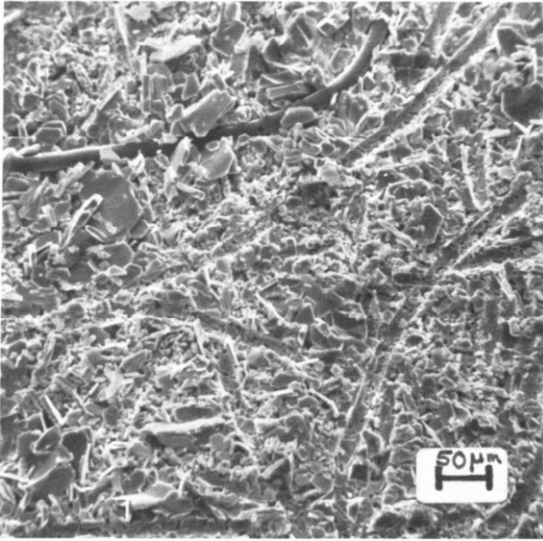
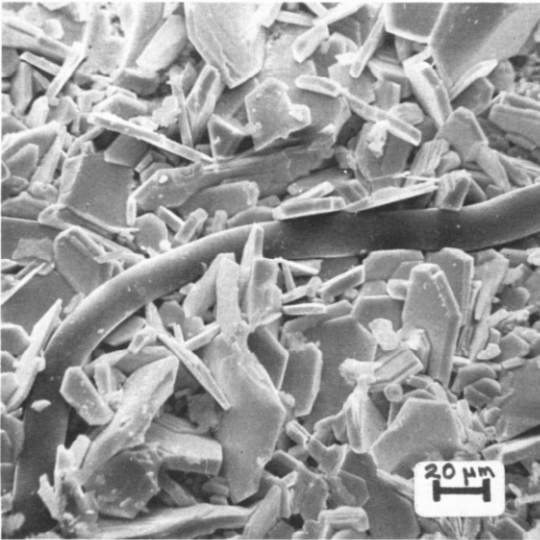


Fig. 2. Comparison of solubility (●) [3] and migration data (x) for  $\text{Cd}(\text{OH})_2$  in 6/7 M KOH as a function of temperature.

An alternative explanation to that of Mayer can be readily found to account for the presence of large quantities of  $\text{Cd}(\text{OH})_2$  in the separator. Elevated temperatures are known to accelerate the recrystallization of  $\beta\text{-Cd}(\text{OH})_2$  on the surface of the negative plate during charge/discharge operation [11] and during storage [12]. This can also lead to imbedding of the separator fibres as indicated in Figs. 3(a) and 3(b). Whilst the be-



(a)



(b)

Fig. 3. (a) Scanning electron micrograph of the surface of a discharged battery plate after several hundred cycles at elevated temperature, showing trapping of separator fibres; (b) as (a) but at higher magnification.

haviour seen in Figs. 3(a) and 3(b) is not desirable it does not necessarily imply that cell failure is imminent. At least in the example cited the large  $\text{Cd}(\text{OH})_2$  crystals were insulating and reluctant to recharge. Furthermore the electrode was removed from a cell giving acceptable performance even after several hundred charge-discharge cycles at 55 °C.

Previous studies in these laboratories [13] have shown that during cycling the active material in the negative plate tends to migrate progressively towards the outer regions of the sinter matrix. At some stage active material grows beyond the confines of the sinter and progresses into the separator by a successive recrystallization process. Thus soluble cadmium species are indeed the route by which  $\text{Cd}(\text{OH})_2$  finds access into the separator. Soluble cadmium species also allow propagation of Cd-dendrites outwards from the negative electrode particularly from rough projections on the surface.

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