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Ideally rechargeable cadmium electrodes for alkaline storage batteries

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$Cd/Cd(OH)_2$ electrodes based on sintered nickel substrate have been developed which show a stabilized capacity-utilisation of 96 ± 2% pf the theoretical value even at the end of fifty cycles of deep discharge at ambient temperatures. Simultaneously, the extent of cadmium migration into the separator on extended cycling or storage has been found to be practically negligible. These improvements have been realized by the incorporation of an alkali-stable colloidal surfactant into the electrode during its fabrication so that both the crystal growth and migration of cadmium hydroxide are suppressed by a protective-colloid action of the surfactant.

1. Introduction

The $Cd/Cd(OH)_2$ electrode is of considerable practical interest due to its widespread use in nickel–cadmium and silver–cadmium alkaline rechargeable battery systems. It has therefore been the object of a large number of investigations. Thus, the electrochemical performance characteristics of the cadmium electrode have been documented under a variety of conditions such as charge–discharge rates, temperatures of operation, modes of storage, charge–discharge cycling, etc. [1–5].

The mechanism of the cadmium electrode reaction in alkaline electrolyte is generally believed to involve the cadmiate ion $[Cd(OH)_3]^-$ species as a dissolved ion intermediate thus.

$$Cd + 3OH^- \rightleftarrows [Cd(OH)_3]^- + 2e \quad (1)$$

$$[Cd(OH)_3]^- \rightleftarrows Cd(OH)_2 + OH^- \quad (2)$$

$$\text{Net reaction: } Cd + 2OH^- \rightleftarrows Cd(OH)_2 + 2e \quad (3)$$

Although the solubility of cadmium hydroxide is small (1.38×10^{-4} M in 30% KOH at 25° C [1]), the charge–discharge reactions (Reaction 3) of the cadmium electrode takes place quite readily due to the fast kinetics of the Reactions 1 and 2.

The involvement of a dissolved ion intermediate in the mechanism of the cadmium electrode reaction leads to two fundamental problems affecting the performance of the electrode, namely, (a) recrystallization and (b) redistribution of cadmium hydroxide active material during charge–discharge cycling.

The recrystallization process occurs due to a natural tendency for growth of both the cadmium hydroxide crystals in contact with the electrolyte saturated with cadmiate ion and also of metallic cadmium in the electrode. The active surface for the electrode is thereby gradually decreased resulting in electrode passivation.

This problem due to recrystallization manifests itself simply as a progressive loss in the capacity of the electrode with an increase in the number of charge–discharge cycles and under certain other conditions. In other words, such a cadmium electrode exhibits a 'capacity fade-out' problem. Since nickel–cadmium cells are usually designed to be positive-limiting, a capacity fade-out of the negative, i.e. cadmium, electrode leads to a negative-limited cell with all its undesirable consequences, especially in a sealed cell.

The problem of redistribution of cadmium hydroxide active material arises as a result of a tendency for nucleation and growth of $Cd(OH)_2$ crystallites to occur towards the open end of the pore, and beyond the electrode itself, due to the crystal growth referred to above which reduces the density of nucleation sites within the pores of the electrode. This culminates eventually as a progres-

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sive displacement of cadmium hydroxide active material from the interior of the porous electrode on the external surface of the electrode and into the separator matrix. The problem is then referred to as that of cadmium migration. Any continuous chain of such particles in the separator contacting the negative electrode will result in the formation of a metallic cadmium dendrite during charge, eventually leading to an internal electronic short with the positive electrode and thereby causing cell failure. Even before such a short circuit is developed, a fall in capacity will occur due to blockage of the pores in the negative electrode by large crystals of cadmium hydroxide, permanent electrolyte flooding of empty pores and, in sealed cells, separator dry-out.

A combination of operational conditions, e.g. high charging and discharge rates, low operating and storage temperatures, storage or open circuit stand only in discharged condition, and prevention of electrolyte carbonation, is generally recommended to minimize the above difficulties. Specific reconditioning procedures are evolved to remedy the difficulties arising from the crystal-growth problem.

Such an operational approach to minimize capacity fade-out and material migration problems of the cadmium electrode, while being helpful, is not always feasible in practice. A more fundamental solution of these problems is therefore desirable.

It is the objective of the present work to report such a solution.

2. Principle

The key factor is to find a way of retarding the growth of crystallites of cadmium hydroxide from the moment of their incorporation into the electrode structure, i.e. during the fabrication of the electrode. If successful, this will not only prevent crystal growth, and hence overcome the capacity fade-out problem, but also suppress the problem of migration of active material since the density of nucleation sites available within the porous electrode itself will be adequate at all times to initiate and sustain crystallization from cadmiate ions in solution.

A simple approach to achieve this result is to incorporate a colloidal surfactant into the electrode, together with the active material, during electrode fabrication so that the surfactant forms a monolayer envelope on the cadmium hydroxide crystallites whose growth rate on ageing is then automatically retarded by a protective colloid action of the surfactant.

The choice of the surfactant additive is governed by the following requirements:

(a) it should be at least partially hydrophilic so that the flow of electrolyte into and away from the interior of electrode-pores takes place readily so as to sustain charge–discharge reactions (Equation 3) without appreciable overpotential

(b) its solubility in the alkaline electrolyte should be negligible so that it is not leached out of the cadmium electrode and eventually oxidized at the positive electrode

(c) it should be completely stable in contact with the alkaline electrolyte

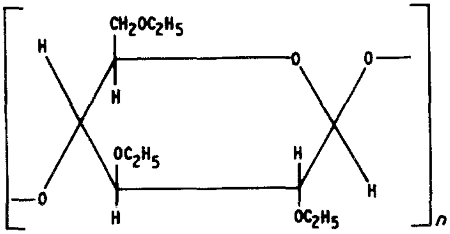
(d) it should be reasonably resistant to oxidation by oxygen which may be present in the vicinity of the electrode, especially in sealed cells with the oxygen recombination cycle

Such an additive has been identified in this work; this is ethyl cellulose. Experimental data presented below confirm the unique application of ethyl cellulose as a crystal-growth retardant and migration suppressor of the cadmium electrode in nickel–cadmium cells.

Ethyl cellulose is a polymeric compound obtained as a product of reaction between alkali cellulose and ethyl chloride. It is a cellulose ether characterized by several unique properties, e.g. insolubility in aqueous solutions, resistance to oxygen and indefinite stability in contact with an aqueous alkaline electrolyte. It has a softening point of about 156° C.

When all the three replaceable hydroxy groups in each anhydroglucose unit of cellulose are replaced by ethoxy groups, the product obtained is the triethyl ether of cellulose with 54.9% ethoxy substitution. The structural formula of this ethyl cellulose with full ethoxy content (substitution value 3) is shown below, corresponding to one anhydroglucose unit of cellulose.

The above compound is less versatile, however, than partially-substituted ethyl cellulose, i.e. one with a substitution value of 2.3 to 2.6 ethoxy groups per anhydroglucose unit (or 44–50%



ethoxy content), due to better solubility and mechanical properties of the latter.

An aqueous dispersion of partially substituted ethyl cellulose is therefore likely to act as a hydrophilic colloidal surfactant.

It was anticipated in the present work that the adsorption of ethyl cellulose on cadmium hydroxide crystallites during electrode fabrication will retard, by a protective colloid-action of ethyl cellulose, any subsequent crystal growth in contact with the alkaline electrote in the cell. Such a retardation of crystal growth will then also assist in the precipitation of any dissolved cadmiate ions within the electrode itself due to the continued availability of nucleation sites for crystallization processes. The hydrophilicity of partially-substituted ethyl cellulose will permit a free passage of electrolyte in and out of the porous electrode during charge–discharge cycling while the extraordinary stability of ethyl cellulose in alkali will ensure its long-time effectiveness. It was also experimentally confirmed in the present work that ethyl cellulose suspension in 30% KOH even when heated to 80° C in air for a few days remains unchanged in all aspects.

3. Experimental aspects

Ethyl cellulose with an ethoxy content of about 48% (corresponding to a substitution value of about 2.45) and viscosity type 100 (i.e. one giving a viscosity of 100 cps in 5 wt% 80:20 toluene: ethanol solvent at 25° C) was used for the following studies*.

Sintered nickel plaques (74 mm x 33 mm x 0.65 mm) used as the porous electrode matrix were manufactured by the slurry process. These plaques were kindly supplied by Messrs Tamil Nadu Alkaline Batteries Limited, Madras. The plaques were degreased, washed, dried and weighed. The plaque porosity was measured using the water inbibition method and found to be 72 ± 1%.

The cleaned plaques were impregnated with cadmium hydroxide using an electrochemical process developed in this laboratory, the main feature of which is a two-step controlled current cathodic polarization of the plaque in an aqueous–alcoholic nitrate–nitrite solution containing cadmium ions. The electrodes, which had a uniform deposition of active material and were completely devoid of any surface precipitate were washed free of nitrate, dried at 60° C in vacuum, weighed and formed in alkali as usual.

The weight gain of the electrodes with respect to cadmium hydroxide was controlled at 2.1 ± 0.1 g cm^{-3} of void volume in the plaque. Since the void volume in each plaque was 1.18 cm^3, the degree of loading of the pores with the active material worked out to 38 ± 2%, assuming that the density of $Cd(OH)_2$ is 4.80 g cm^{-3}. This degree of loading is similar to the present commercial practice for sealed nickel–cadmium cells.

The electrodes were subjected individually to cycle-life tests in 30% KOH under flooded electrolyte conditions, with counter electrodes of sintered nickel positive electrodes of excess capacity on either side of the test electrode. The capacity of each test electrode was measured by noting the potential of the test electrode under galvanostatic discharge against a $Cd/Cd(OH)_2$ reference electrode which was provided with a Luggin tip aligned close to the centre of the electrode.

The cycle-life test regime was $C/2$ rate charge for 130 min and $C/2$ discharge to a cut-off at + 1.0 V vs Cd-reference electrode at ambient temperature (30 ± 5° C). This corresponds to a 100% depth of discharge in each cycle. At the end of fifty such charge–discharge cycles the electrodes were over-discharged until oxygen evolution occurred uniformly on the surface. The electrodes were then taken out, washed, dried in vacuum at 60° C and weighed. The weight of the active material found at this stage was taken as the basis for the calculation of capacity-utilization reported in the paper. Such a procedure eliminates any possibility of incorrect capacity data being recorded due to any unreacted (metallic) cadmium in the active material.

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* This compound is commercially available, for example, as Ethyl Cellulose N-100 from Hercules Co., USA.

The introduction of ethyl cellulose into the cadmium hydroxide active material was carried out in three different ways:

1. (Control): Electrodes were prepared by electrochemical impregnation without any ethyl cellulose addition, washed, dried and formed as stated before.

2. Electrodes prepared by electrochemical impregnation were immediately dipped, after being taken out of the impregnation bath, in a well-stirred solution similar in composition to this bath except that it also contained ethyl cellulose (about 0.1 $\mathrm{g\,l^{-1}}$). The electrodes were left in the solution on open circuit for 15 min, and then processed as usual.

3. Electrodes prepared by electrochemical impregnation were dipped after washing and drying (but before formation) in a 2 wt % solution of ethyl cellulose in 80:20 toluene:ethanol mixed solvent. The electrodes were soaked thus for 5 min, taken out, dried at 60° C and then subjected to formation.

4. Electrodes prepared as in Case 2 were coated, after washing and drying (but before formation), with another ethyl cellulose coating from a mixed organic solvent as in Case 3.

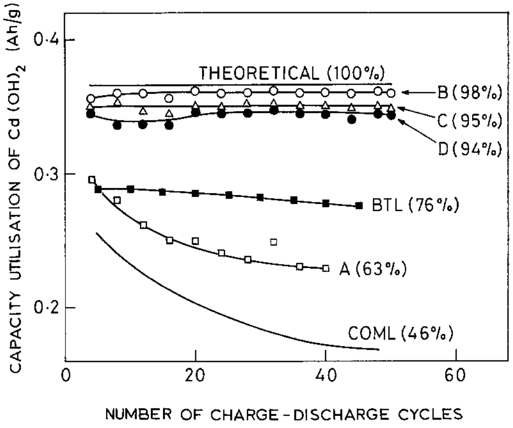

Fig. 1. Dependence of capacity utilization of sintered-plate Cd/Cd(OH)$_2$ electrode on the number of charge-discharge cycles with 100% depth of discharge in each cycle at room temperature. A – electrodes prepared in this work without any additive (Control); B – electrodes prepared with a coating of ethyl cellulose by immersing in aqueous–alcoholic cadmium nitrate–sodium nitrate bath saturated with ethyl cellulose immediately after electrochemical impregnation; C – electrodes prepared with a coating of ethyl cellulose by immersing in a 2% solution of ethyl cellulose in toluene–ethanol mixed solvent; D – electrodes prepared with a coating of ethyl cellulose by both B and C (in that order). BTL are electrodes from proprietary process of Bell Telephone Laboratories [2]. COML are electrodes from standard commercial practice [2].

A minimum of three electrodes were subjected to each test. The mean deviation in capacity of different electrodes in each case was 5% or less, except in Case 1, i.e. without ethyl cellulose treatment, where the mean deviation was about 15%.

For studies on the cadmium-migration problem nickel–cadmium cells each of 3 Ah capacity were assembled with a non-woven nylon separator covering each electrode on all sides and inserted into a tight-fitting ABS plastic container, the lid (also of ABS) which was provided with terminal feed-throughs and a low pressure vent, being sealed to the container with ABS cement. The electrolyte was 30% KOH in a quantity just sufficient to cover the electrodes at the end of charge. Separate cells were assembled using ethyl cellulose-treated, and ethyl cellulose-free cadmium electrodes. The cells were subjected to a random cycling including overcharge and full discharge over a period of about a year.

4. Results and discussion

4.1. *Electrode capacity studies*

The faradaic efficiency of cadmium electrodes with and without the surfactant additive is shown in Fig. 1 as a function of cycle life under deep discharge conditions.

It may be seen from Fig. 1 that the ethyl cellulose-treated cadmium electrodes (B–D) show an excellent faradaic efficiency which is within 3% of the theoretical value even after fifty cycles of deep discharge between cycles. In other words, not only is the utilization efficiency of the active material nearly ideal but the capacity fade-out problem is also practically non-existent. Moreover, the capacity spread among electrodes prepared and cycled under otherwise identical conditions is least for ethyl cellulose-treated electrodes (B–D) and highest for conventional (uncoated) electrodes (A).

Literature evidence (Fig. 1) indicates also that the stabilized capacity of commercial sintered plate cadmium electrodes on charge–discharge cycling is only 40–50% of the theoretical value, although electrodes obtained from proprietary

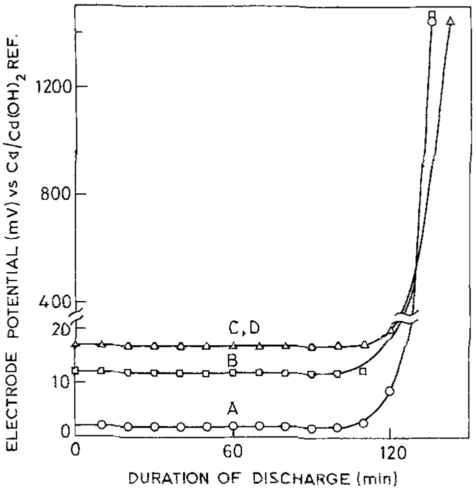

Fig. 2. Single electrode potential vs time during $C/2$ rate discharge of sintered plate $Cd/Cd(OH)_2$ electrodes. A, B, C and D as for Fig. 1.

processes have been quoted [6, 7] to give a stabilized capacity of 75–85% of the theoretical value. All these values are in contrast to the stabilized capacity realized by the present method, namely, 96 ± 2% of the theoretical value.

The slight variation among the different ethyl cellulose-treated electrodes may be attributed to different thicknesses of adsorbed ethyl cellulose layer produced by the several methods adopted.

4.2. *Single electrode potential studies*

The variation of the potential during discharge of cadmium electrodes prepared with and without ethyl cellulose treatment is shown in Fig. 2.

It follows from Fig. 2 that any ohmic drop caused by the adsorbed layers of ethyl cellulose on cadmium hydroxide crystals of the test electrodes (B–D) is only 10–20 mV at the $C/2$ rate discharge. The lowest observed value of 10 mV is obtained with Type B ethyl cellulose-treated electrode which shows, at the same time, the best capacity performance (Fig. 1) along the three types of ethyl cellulose-treated electrodes.

4.3. *Studies with assembled nickel–cadmium cells*

Cells prepared as described under experimental aspects were subjected to random cycling and storage conditions over a period of a year, then cut open and examined visually. In cells with ethyl cellulose-treated cadmium electrodes, the separator could be detached from the electrodes without any difficulty, there was no smudging, discolouration or presence of active material in the separator, and the external surface of the electrode was completely free of cadmium hydroxide scales. On the other hand, in cells with untreated cadmium electrodes, the separator could not be detached easily from the electrodes, there was significant smudging, grey colouration and presence of active material in the separator; the external surface of the cadmium electrodes also showed the presence of white and grey cadmium hydroxide crystals.

It is evident that the migration of active material from the cadmium electrode is suppressed to a large extent or even eliminated altogether in cells with ethyl cellulose-treated cadmium electrodes.

It is important to note that the above beneficial effects of ethyl cellulose are lost to a large extent if the electrodes are dried at high temperatures in air or subjected to severe overdischarge. Also, too thick a coating of ethyl cellulse will lead to some loss in available capacity due to the large ohmic resistance of the film.

5. Conclusions

Two basic problems of the cadmium electrode in nickel–cadmium cells, namely, capacity fade-out on cycling and active material migration into the separator are practically eliminated by a controlled incorporation of ethyl cellulose into the electrode during fabrication. The mechanism of action of ethyl cellulose is one of a protective colloid adsorbed on the cadmium hydroxide crystallites thus preventing their growth and subsequent migration. The chemical inertness of ethyl cellulose in contact with alkaline electrolyte even over extended periods of time ensures that the beneficial effects of ethyl cellulose-treated cadmium electrodes in nickel–cadmium cells will be long-lasting.

Acknowledgement

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