EFFECT OF TETRA-ALKYL AMMONIUM COMPOUNDS ON THE PERFORMANCE OF ELECTRODES OF SINTERED PLATE NICKEL– CADMIUM CELLS

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Summary

Several cycles of impregnation and forming are required to achieve the required weight of active material in the sintered electrodes of nickelcadmium batteries. Certain surface active agents were added to the impregnating solution with a view to reducing the number of cycles of impregnation. The reduced surface tension of the solution was to have increased the quantity of intake of the solution by the sintered matrix. A very striking result was, however, observed in the performance characteristics of the plates prepared with the addition of a quarternary ammonium compound to the impregnating solutions. These are presented and explained on the basis of the particle size of the active material.

Introduction

It is well known that in the preparation of plates for sintered plate nickel-cadmium batteries the sintered matrix is impregnated with an aqueous solution of nickel or cadmium salts to produce positive or negative plates respectively. Several cycles of impregnation and forming are required to achieve the required weight of active material in the plate. An addition of certain surface active agents was made to the impregnating solution for a possible reduction in the surface tension so that an increased quantity of the solution may be impregnated in the pores of the sintered matrix. Several such surface active agents were tried out, of which quarternary ammonium compounds with a typical formula:

$$\begin{bmatrix} \mathbf{R_1} \\ | \\ \mathbf{R_4} \cdots \mathbf{N} \cdots \mathbf{R_2} \\ | \\ \mathbf{R_3} \end{bmatrix}^+ \mathbf{X}^-$$

for example cetyl trimethyl ammonium compounds, were found to have a marked influence on the performance of the plates [1].

The performance characteristics at high rates of discharge were more pronounced than at low rates of discharge, and hence also the utilization efficiency was found to be much higher at high rates of discharge than at lower rates.

Experimental

The experimental cell comprised one positive plate and two negatives for a study of the characteristics of the positive plate and vice versa for the negative plates, so that the plate under investigation limits the capacity. The plates were prepared by sintering carbonyl nickel powder to a punched nickel plated, steel grid of dimension 7.5 cm \times 6 cm. The thickness of the plates was 0.8 ± 0.05 mm and the porosity of the sintered plaque only prior to forming ranged between 60 and 65%. The impregnating solution was prepared from AR grade nickel nitrate for the positive and cadmium nitrate for the negative. The quarternary ammonium compound was made into a solution before it was added to the respective solutions to be used for impregnation. A vacuum impregnation method, which is generally adopted for preparing the plates, was also adopted in this investigation. For comparison an equal number of blanks was also prepared from impregnating solutions without the addition agent. Each positive plate contained 4 ± 0.2 g of active material and each negative plate contained 5 ± 0.2 g of active material. The theoretical capacities of the positive and negative plates were around 1.2 ampere hours and 1.95 ampere hours respectively, depending on the exact weight of the active material impregnated.

The plates under study were assembled against two plates of the opposite polarity using nylon cloth as the separator. The plates were assembled in air-tight containers and protected from the atmosphere by pressure vents. Initial conditioning of the cells consisted in carrying out charging at the 5 h rate for seven hours and discharging at the 5 h rate. After 3 such conditioning cyles the average capacity obtained was considered as the capacity of the cell, designated as C. The end point of the discharge was determined by the potentials of the respective plates measured against an Hg/HgO reference electrode. The positive plate was considered to have discharged when it reached a potential of +0.2 V for low rates and 0.1 V for high rates of discharge and similarly for the negative when it reached a potential of -0.75 V at low rates and -0.6 V at high rates with respect to the reference electrode. The discharges were carried out at the $C/5 \ 1C, \ 5C$ and 10C rates. The current, voltage and time were measured with standard measuring equipments.

Results and discussion

The performance of the positive plates at different rates is shown in Figs. 1 to 4. The potential values are plotted against time of discharge. Sim-



Fig. 1. Discharge curve for the positive plate at C/5 rate. \circ , Plate with addition agent; \bullet , plate without addition agent.



Fig. 2. Discharge curve for the positive plate at C rate. \circ , Plate with addition agent; \bullet , plate without addition agent.

ilar performance curves for the negative plates are given in Figs. 5 to 8. At low rates there is considerable variation in potential with time between the plate with addition agent and the blank. But at high rates the difference in potential between the two is more or less uniform throughout the discharge, thus showing a resistive component in the case of both the positive and the negative plates. The influence of the addition agent has been found to be more pronounced on the negative than on the positive plate.



Fig. 3. Discharge curve for the positive plate at 5C rate. \circ , Plate with addition agent; \bullet , plate without addition agent.



Fig. 4. Discharge curve for the positive plate at 10C rate. \circ , Plate with addition agent; •, plate without addition agent.

The utilization efficiencies of the positive and negative active materials at different rates of discharge are shown in Figs. 9 and 10 respectively. From the Figs. it can be seen that there is a marked difference in the efficiency especially at high rates. For the negative this variation is pronounced even at the 1C rate and above whereas in the case of the positive plate it is perceptible only at the 5C and 10C rates. The utilization efficiency for the positive plates with the addition agent was found to be 49% at the 10C



Fig. 5. Discharge curve for the negative plate at C/5 rate. \circ , Plate with addition agent; \bullet , plate without addition agent.



Fig. 6. Discharge curve for the negative plate at C rate. \circ , Plate with addition agent; \bullet , plate without addition agent.

rate, as against 23% for the blank, which is half of the former. Similarly the negative shows an efficiency of 22% at the same rate as compared to 13% for the blank.

The photomicrographs of the active material scrapped from the positive and negative plates as well as for the material precipitated from solutions with and without addition agent are shown in Figs. 11 and 12,



Fig. 7. Discharge curve for the negative plate at 5C rate. \circ , Plate with addition agent; \bullet , plate without addition agent.



Fig. 8. Discharge curve for the negative plate at 10C rate. \circ , Plate with addition agent; \bullet , plate without addition agent.

respectively. The material formed without the addition agent is found to be lumpy as can be seen from the Figs. Photomicrographs of active material precipitated from nickel salts and cadmium salts containing the addition agents were also taken and were found to be similar to the ones shown in the above Figs.

The fact that the coefficient of utilization at normal rates such as the five hour rate does not show much variation and is high at high rates of discharge suggests that more active material is available for the reaction in the plates made with the addition agent than in the blank. This is also



Fig. 9. Variation of utilization efficiency with discharge current-positive plate. \circ , With addition agent; \bullet , without addition agent.



Fig. 10. Variation of utilization efficiency with discharge current-negative plate. \circ , With addition agent; \bullet , without addition agent.

brought out by the exhibition of a resistive component in the discharge curves as discussed above. This may be due to the lumpy nature of the active material formed without the addition agent as is evident from the photomicrographs.

The effect of the addition of tetra-alkyl ammonium compounds on the reduction of the number of impregnation cycles has not been significant, whereas there is a striking influence of the addition agent on the performance of the cells, especially at high rates of discharge. Further work on this aspect is in progress and will be covered in a future paper.



(c)

Fig. 11. Photomicrograph of positive active material × 150. (a) Material scraped from plates without the addition agent; (b) material scraped from plates with the addition agent; (c) material precipitated from solution without the addition agent; (d) material precipitated from solution with the addition agent.



(a)

(b)

Fig. 12. Photomicrograph of negative active material $\times 150$.



(c)

(d)

Fig. 12. Photomicrograph of negative active material \times 150. (a) Material scraped from plates without the addition agent; (b) material scraped from plates with the addition agent; (c) material precipitated from solution without the addition agent; (d) material precipitated from solution with the addition agent.

Reference

1 Indian Patent No 716/72.