

# On the growth of $\text{Li}_2\text{CO}_3$ dendrites in nickel–cadmium industrial batteries

Ulrik Palmqvist <sup>\*</sup>, Rune Sjövall

*Saft AB, Jungnergatan, PO Box 709, SE-572 28 Oskarshamn, Sweden*

Received 10 August 1998; accepted 19 January 1999

## Abstract

A large amount of  $\text{Li}_2\text{CO}_3$  dendrites has been detected on positive electrodes in Ni–Cd industrial pocket plate batteries, intended to work in stationary applications, after 3 years in float charge. The lattice parameters were refined to  $a = 8.353(1) \text{ \AA}$ ,  $b = 4.974(1) \text{ \AA}$ ,  $c = 6.194(1) \text{ \AA}$  and  $\beta = 114.6(1)^\circ$  [monoclinic], which is in complete agreement with structural data reported in the literature. Oxidation of graphite present in the positive active material is enhanced at elevated temperatures, and at high anodic potentials. This results in an extremely high carbonate concentration in the active material, as well as in the electrolyte. The high carbonate content, in combination with the relatively high lithium concentration present in both electrolyte and positive electrode, is very likely to be the reason for the formation of the  $\text{Li}_2\text{CO}_3$  dendrites. As this process continues, agglomerates of the dendrites in combination with attached  $\beta\text{-Cd}(\text{OH})_2$  and graphite may generate short circuits between the positive and the negative electrodes. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:*  $\text{Li}_2\text{CO}_3$ ; Nickel–cadmium; Battery

## 1. Introduction

From a manufacturer's point of view, it is of utmost importance to maintain a high quality product. Despite this, the product might sometimes be rejected and sent back due to different failures. One type of failure that occur in pocket plate Ni–Cd alkaline batteries is caused by short circuits between the electrodes. In the literature, this failure is explained either by migration of  $\text{Cd}(\text{OH})_2$  or by Cd dendrite growth. The former theory concerns the electrophoretic migration of  $\text{Cd}(\text{OH})_2$  active material through the perforated strips of the pockets during charge/discharge cycling [1]. If the conditions are favorable, a bridge of negative active material might be formed between the electrodes. This theory has, however, been criticized by several workers [2]. The latter theory, in the literature considered as the more likely one, concerns the generation

of Cd dendrites [2,3]. The dendrites are formed as a consequence of the dissolution–precipitation mechanism occurring at the negative electrode during charge/discharge. This kind of short circuit formation is described in detail by Sathyanarayana [3].

In the present paper, electrodes from rejected pocket plate Ni–Cd cells have been studied by X-ray diffraction and by optical- and scanning electron microscopy in order to find an explanation of the battery failure. It should be emphasized that the positive active material contains reasonable amounts of graphite in order to enhance the electrical conductivity and the cell Li ions in order to increase the battery life [4,5]. The investigated cells had been float-charged in a railway application during 3 years.

## 2. Experimental

Ten rejected cells were tested electrically. The concentration of carbonate-, hydroxide- and lithium ions in the electrolyte was determined by ordinary acid–base titration

<sup>\*</sup> Corresponding author. Inorganic Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91 Stockholm, Sweden. Tel.: +46-8-674-75-52; Fax: +46-8-15-21-87; E-mail: ulrik@inorg.su.se

and by atomic absorption spectrometer measurements (Varian; AA 1275).

Four cells were dismantled and investigated by means of optical and scanning electron microscopy (JEOL; JSM 840-A). Analyses of electrode active material and sludge were made on an X-ray fluorescence spectrometer (Philips; PW2040) and an X-ray powder diffractometer (Philips; PW3040).

The unit-cell parameters of the transparent, needle-like  $\text{Li}_2\text{CO}_3$  crystals were obtained from powder photographs taken with a Guinier–Hägg focusing camera ( $\text{Cu K}_\alpha$  radiation,  $\lambda = 1.540598 \text{ \AA}$ ). Least-squares refinement of the cell parameters was based on 21 single indexed lines. For the crystallographic analysis, the programs, TREOR [6] and PIRUM [7], were used.

### 3. Results and discussion

In the electrolyte of the rejected cells, extremely high carbonate concentrations were detected with values ranging from 120 to 250 g/l (given as  $\text{K}_2\text{CO}_3$ ). According to Falk and Salkind [4], the amount of carbonate should in general not exceed 80 g/l. Furthermore, the  $\text{LiOH}$  concentration in the electrolyte of the cells above was in the range 10 to 12 g/l.

Electrically, it was shown that all 10 rejected cells failed in the short-circuit mode. Dismantled cells exhibited large salt-like islands (Fig. 1), up to several centimeters in size, on both sides of the positive electrodes. These islands consisted of transparent needles (dendrites) of  $\text{Li}_2\text{CO}_3$

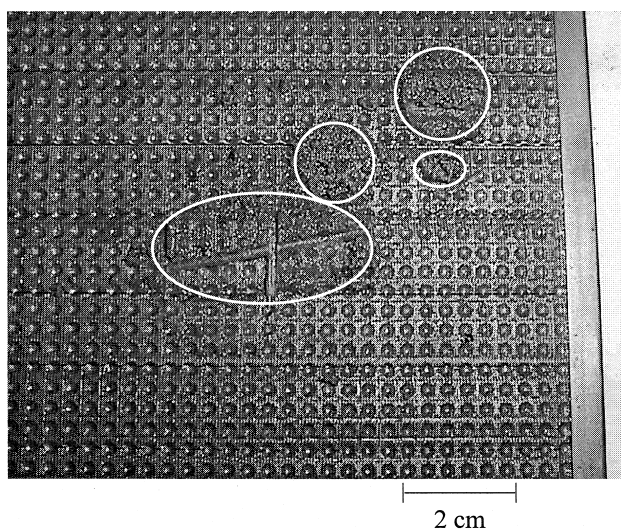


Fig. 1. Optical micrograph showing islands (within white borders) of agglomerated  $\text{Li}_2\text{CO}_3$  crystals mixed with small amounts of  $\beta\text{-Cd(OH)}_2$  and graphite. An imprint from the separator (cross) is seen on the largest agglomerate. The circular areas ( $\varnothing \approx 2 \text{ mm}$ ) are imprints from the ball rolling process.

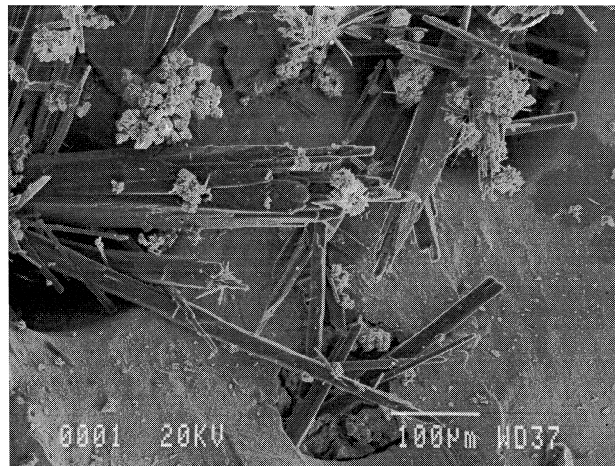
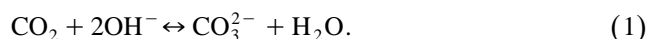


Fig. 2. Electron micrograph showing  $\text{Li}_2\text{CO}_3$  dendrites growing through the holes of the strip of the positive electrode. (The clusters of prismatic crystals consist of potassium hydroxide, which has been formed during dismantling of the cell.)

crystals, which partially were covered with small  $\beta\text{-Cd(OH)}_2$  particles. The length of the  $\text{Li}_2\text{CO}_3$  dendrites reached several millimeters. The observed cell dimensions for  $\text{Li}_2\text{CO}_3$  were  $a = 8.353(1) \text{ \AA}$ ,  $b = 4.974(1) \text{ \AA}$ ,  $c = 6.194(1) \text{ \AA}$  and  $\beta = 114.6(1)^\circ$  [monoclinic]. These values agree completely with those reported in the literature [8–11]. Among the salt-like agglomerates, traces of graphite could be detected as well. On the negative electrode surfaces, black particles consisting of  $\beta\text{-Cd(OH)}_2$ , graphite and cadmium could also be found. The sludge was mainly composed of  $\beta\text{-Cd(OH)}_2$  and graphite. Rather surprisingly, no  $\text{Li}_2\text{CO}_3$  was detected in the sludge.

From visual inspection, it became obvious that the large islands of agglomerated  $\text{Li}_2\text{CO}_3$  crystals, mostly located at the horizontal bars of the polypropylene separators (Fig. 1), had caused the short circuits between the electrodes. Furthermore, it was evident that the dendrite growth started at the exterior surface of the positive electrodes (Fig. 2). Since this phenomenon has not been reported elsewhere, it will be further discussed in the following section.

During overcharging at constant voltage, the graphite in the positive active material will be partly oxidized and carbonate ions,  $\text{CO}_3^{2-}$ , will be formed in the alkaline electrolyte according to the simplified reaction:



The concentration of  $\text{CO}_3^{2-}$  will increase in the pores of the positive active material, as well as in the electrolyte, as a function of time during overcharging. The higher the float voltage and temperature, the higher is the rate of  $\text{CO}_3^{2-}$  formation. High carbonate concentration, in combination with a relatively high lithium content in the positive active material, favors the precipitation reaction:



The dendrite formation is probably a random process, governed by the occurrence of nucleation sites, where  $\text{Li}_2\text{CO}_3$  can grow from the exterior surface of the active material of the positive electrode towards the bulk electrolyte, as displayed in Fig. 2. In particular, it seems that the horizontal bars of the separators are good nucleation sites (Fig. 1). As the precipitation process continues, more and more  $\text{Li}_2\text{CO}_3$  are formed on the exterior surface of the positive electrode strips, and finally, short circuits will be established.  $\text{Li}_2\text{CO}_3$  is, however, a non-electronic conductor and cannot alone give rise to the internal short circuits. But since the dendrites are found to be partly covered by  $\beta\text{-Cd(OH)}_2$  and graphite, this will be possible. The  $\beta\text{-Cd(OH)}_2$  and graphite particles are liberated from the electrodes during charge/discharge.

#### 4. Conclusion

It is obvious that there is an increased risk for short circuit generation due to  $\text{Li}_2\text{CO}_3$  precipitation after prolonged float charging at high potentials and/or at elevated temperatures in the Ni–Cd pocket plate system discussed.

#### Acknowledgements

We are grateful to MSc Per Viklund, Inorganic Chemistry 2, Lund University, Sweden, for performing SEM analyses.

#### References

- [1] S.W. Mayer, *J. Electrochem. Soc.* 123 (1976) 159–162.
- [2] R. Barnard, *J. Appl. Electrochem.* 11 (1981) 217–237.
- [3] S. Sathyanarayana, *Power Sources* 7 (1979) 141–151.
- [4] S.U. Falk, A.J. Salkind, *Alkaline Storage Batteries*, Wiley, New York, 1969.
- [5] E.J. Rubin, R. Baboian, *J. Electrochem. Soc.* 118 (1971) 428–433.
- [6] P.-E. Werner, L. Eriksson, M. Westdahl, TREOR, a semi-exhaustive trial-and-error powder indexing program for all symmetries, *J. Appl. Crystallogr.* 18 (1985) 367–370.
- [7] P.-E. Werner, A Fortran program for least-squares refinement of crystal-structure cell dimensions, *Arkiv Kemi* 31 (1969) 513–516.
- [8] J. Zemann, *Acta Cryst.* 10 (1957) 664–666.
- [9] H. Effenberger, J. Zemann, *Z. Kristallogr.* 150 (1979) 133–138.
- [10] Y.-Y. Lin, H.-Q. Zhang, M.-P. Zheng, *Chin. Sci. Bull.* 35 (1990) 489–492.
- [11] International Center for Diffraction Data: Powder Diffraction File #22-1141.