

The influence of discharge time on post-partial discharge gassing of zinc powder

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Abstract

Gas evolution in primary alkaline cells depends on discharge time. This dependence can be so strong that acceptable volumes of gas are evolved in cells when discharged over relatively long periods, whereas shorter times may lead to gassing beyond the limits of the cell design. The dependency of gassing on discharge time was investigated for a number of commercial cells and for different zinc-alloy powders. An indication of a relation between certain alloying elements and the gas evolution at short discharge times was found. The most important result of the investigations, however, was the development of a modified zinc powder production process which leads to zinc powders with reduced gas evolution rates for both short and long discharge times. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In the literature, and particularly in the patent literature, there can be found many investigations on the gas evolution of zinc powder in primary alkaline cells, since the formation of hydrogen gas in cells has been one of the major problems in the manufacture of primary zinc/manganese alkaline cells.

As the rate of gas evolution influences the useful life of a cell, and is therefore one of the most critical characteristics of zinc powder, many ways have been found and described to lower the gas evolution. However, despite the description of zinc-alloy powders which lead to less gas evolution, little has been published on the mechanism causing the gas evolution or on the mechanism which reduces the gas evolution.

With cells containing amalgamated zinc powder, it was quite simple to assume that the hydrogen overvoltage of mercury was the main factor in reducing the gas evolution. With mercury-free zinc powders, the situation is much more complex, another complexity arises from the fact that the gas evolution is evidently quite different for fresh zinc powder in cells as compared to partly discharged zinc powder in cells. Further, little of the published work contains data on gas evolution as a function of state of

discharge. This paper concentrates on this aspect of the behaviour of zinc powders.

2. Gas evolution in commercial cells

Various makes of LR6 cells were bought and discharged under a constant load of 3.9 Ω . The discharge time was varied from 0 min (undischarged) to 480 min for totally discharged cells. Then each of the cells was placed into a graduated centrifuge tube filled with paraffin oil, which was set with the closed side up into a paraffin filled beaker, so that any gas coming from the cell had no other way to go than to the closed top of the centrifuge tube. The beakers went into a temperature controlled oven and were left there for exactly 7 days at a temperature of 70°C. Then the beakers were removed, cooled to ambient temperature and the amount gas collected in each tube was recorded.

The next step was to remove the cells from the paraffin and to open them under water so that the gas from inside the cells could be collected in a burette. This somewhat complicated method enabled the determination of gas evolution in cells even for those cases where there was gas leaking from the cells through a designed vent.

The total volume of gas collected in the cells was plotted against discharge time and these data are in Fig. 1. The data are for two sets, each of nineteen LR6 cells. The

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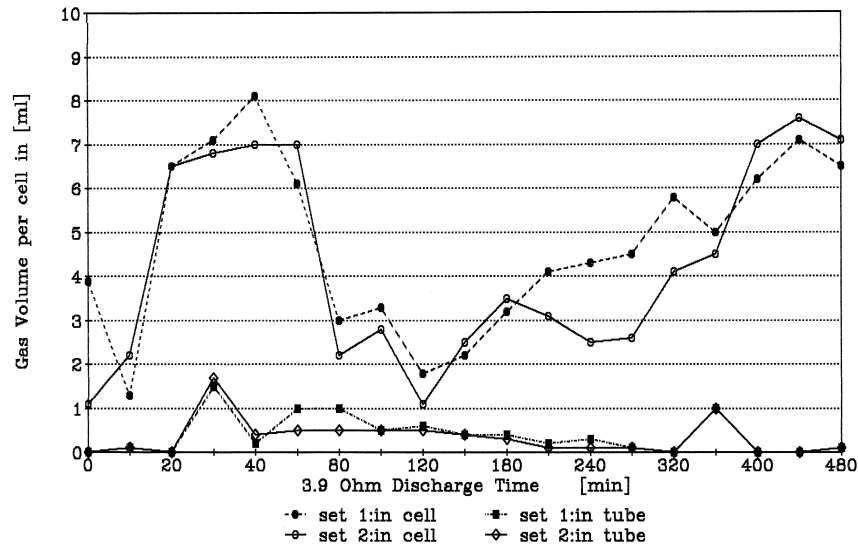


Fig. 1. Gas evolution against time-into-discharge for two sets of LR6 cells, each containing 19 cells. Volumes collected in tubes and from within cells are shown separately.

legend separately identifies the data for the amount of gas found in the centrifuge tubes, i.e., the amount of gas which emanated from the cells during the storage time, and the amount of gas found after opening the cells. As the figure shows there is not much gas coming out of the cells and the scatter of data for the amount collected in the centrifuge tubes is small.

All data points have been connected, as it is evident that there are not enough data to form a smooth curve. However the comparison of the data for the two sets of cells demonstrates that the apparent correlation of rate of gassing on discharge time is typical for this type of cell. The data do not reveal in how far the gas evolution is due only to the zinc powder: it may be possible that the anode current collector used in this make of cell has some influence on

the gas evolution. But this aspect is not part of this paper, the importance of the test was to show that there can be a strong gas evolution–time of discharge relation. Fig. 2 shows data found for different makes of LR6 cells. All data are the average of two cells for each discharge time and they are the sum of the gas volume which emanated from the cell and the volume which remained in the cell. The legend gives abbreviations for the various makes of cell tested.

The figure shows that all the cells investigated exhibit a gas evolution dependence on discharge time. The gas evolution increases as the discharge approaches totality, and since the effects can be caused by the anode current collector, that part of the figure is not discussed any further.

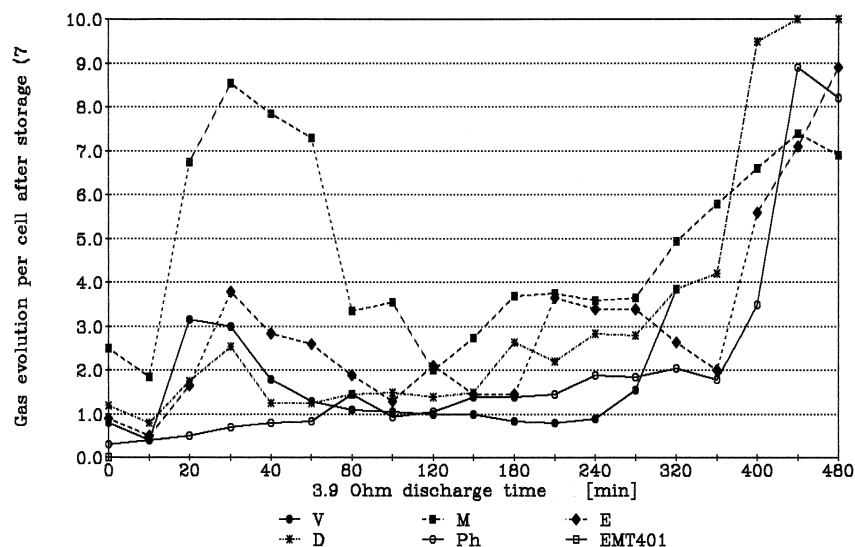


Fig. 2. Total gas evolution against time-into-discharge from pairs of various makes of LR6 cells.

Fig. 2 also shows that the gas evolution can be very high early into the discharge but it is difficult to find an approach to zero gassing at any time during the discharges. In other words, it is difficult to identify an area where the gas evolution for one discharge time can be taken as a reliable means for quality control, as can be done in the LR14 size of cell. This will be discussed later in the paper, and Table 1 gives the results of the chemical analysis performed on the zinc powder gels extracted from such cells.

It should be noted that the analysis was done on the gel, therefore it was not possible to differentiate between elements in the zinc powder and elements in the gel.

As was shown in Fig. 2, most of the cells investigated exhibit a maximum in gas evolution as a function of discharge time, but so far it has not been possible to link this maximum to any specific element present in the zinc powder.

3. Gassing behaviour of various zinc alloy powders

Some experiments have been carried out in order to find out whether there is a relation between the observed maximum and the alloying composition of the zinc powder.

For these experiments LR14 cell assemblies from one manufacturer have been used. Zinc powder gels were made according to one standard formulation:

- 67 wt.% zinc powder
- 0.5 wt.% Goodrich Carbopol 9.42 gelling agent
- 32.5 wt.% electrolyte type E2.

The electrolyte type E2 has the composition of 40% KOH 'Arragonesas flakes, technical grade' and 4% zinc oxide 'Grillo pharmaceutical grade'.

Table 1

Analysis of zinc powder gels from the cells in Fig. 2: all elemental compositions in ppm

Element	Abbreviation for make of cell				
	V	M	E	D	Ph
Pb	470	540	< 30	< 30	< 30
In	140	400	380	280	770
Bi	66	300	200	220	470
Ca	< 10	< 10	140	< 10	n.d.

Zinc powder and gelling agent were mixed in a 250 ml polythene bottle by tumbling for 5 min. Then the electrolyte was added and immediately mixed with the zinc powder by vigorous shaking. Subsequently the bottles were transferred into a vacuum chamber, evacuated to less than 60 mbar and stirred for 15 min. The gel was allowed to mature for 4 h at ambient temperature.

LR14 cells were filled with 5 ml free electrolyte and 16 g of zinc gel by means of Hibar pumps. The cells were closed and after another a maturing time of 1 h discharged continuously through a load of 2 Ω for various periods up to full discharge. Following discharge the cells were stored for 7 days at 70°C and the amount of gas measured, exactly according to the procedure given in clause 2 for the LR 6 cells.

Fig. 3 gives the results found when using an amalgamated zinc powder of the composition: Zn; 500 ppm Pb; surface amalgamated to 0.15% Hg. Surprisingly enough, the data show that even for lightly amalgamated zinc powder, the gas evolution may depend on time into discharge.

Fig. 4 gives results found when using the zinc alloy: Zn; 500 ppm Pb:300 ppm Bi:300 ppm In. The maximum point of gas evolution becomes quite evident. Another

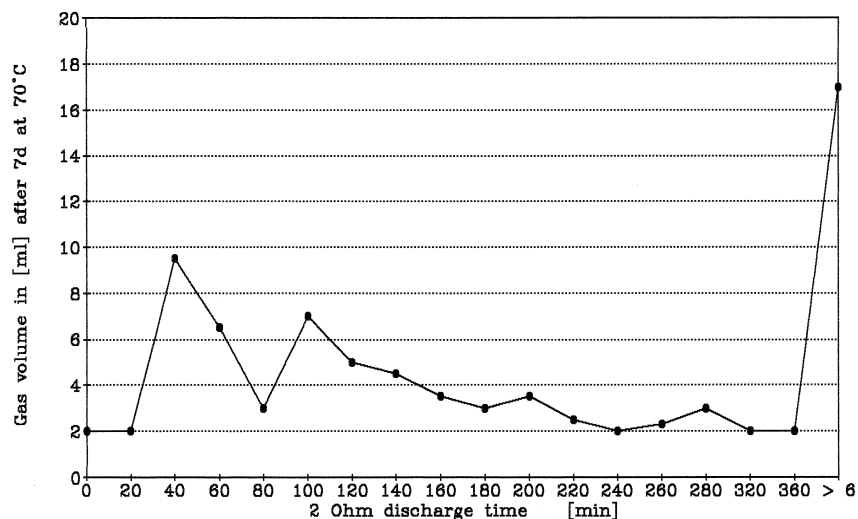


Fig. 3. Total gas evolution against time-into-discharge from an LR14 cell containing an anode of composition: Zn + 500 ppm Pb and surface amalgamated to 1.5% Hg.

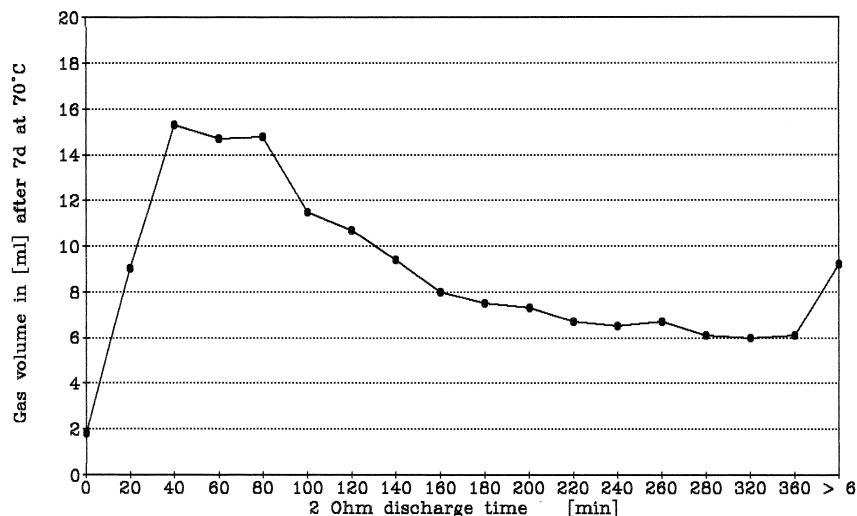


Fig. 4. Total gas evolution against time-into-discharge from an LR14 cell containing an anode of composition: Zn + 500 ppm Pb:300 ppm Bi:300 ppm In.

interesting aspect becomes obvious and this is that the differential of gas volume to time of discharge becomes very small at discharge times between 240 and 300 min. This was also seen in many other investigations and this, say gas evolution at 270 min into the discharge, can be used to characterise the zinc powder for production quality control.

Fig. 5 gives the data of the alloy: Zn; 500 ppm Pb:300 ppm Bi:300 ppm In, and includes the results of the gas evolution when 300 ppm of indium oxide was mixed as a dry powder into the gel.

The data indicate that the additional indium present in the gel not only may lead to increased gas evolution but also may increase the relative maximum of the gas evolu-

tion. This result is a first indication that the indium has a strong influence on the relative maximum of the gas evolution as a function of discharge time.

Fig. 6 gives the results from LR14 cells containing three different alloys:

- (a) Zn; 500 ppm Pb:300 ppm Bi:300 ppm In.
- (b) Zn; 500 ppm Pb:300 ppm Bi:300 ppm In + 300 ppm indium oxide
- (c) Zn; < 30 ppm Pb:250 ppm Bi:800 ppm In.

and demonstrates the very strong maximum of gas evolution early in the discharges for the lead-free alloy containing 800 ppm of indium.

The curves for the alloy Zn; 500 ppm Pb:300 ppm Bi:300 ppm In, and for this alloy when 300 ppm of indium

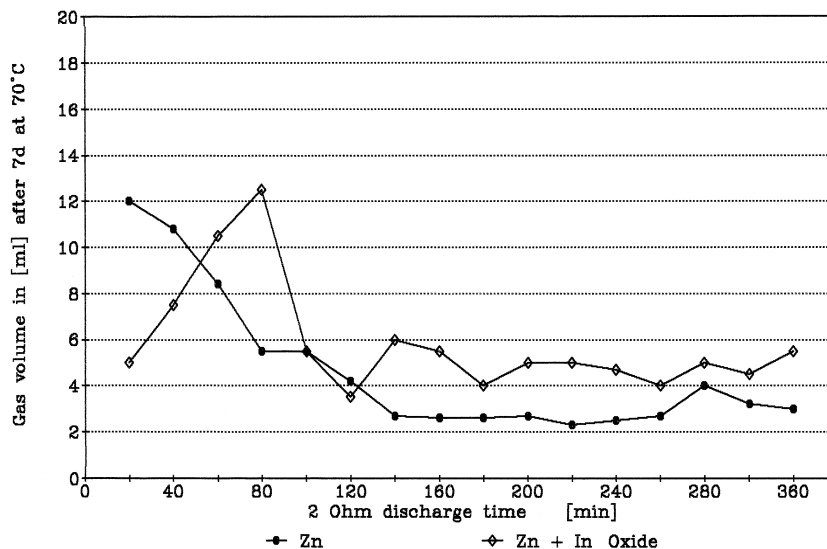


Fig. 5. Total gas evolution against time-into-discharge from two LR14 cells containing anodes of composition: Zn + 500 ppm Pb:300 ppm Bi:300 ppm In. One cell contained an additional 300 ppm of indium oxide, mixed as dry powder into the gel.

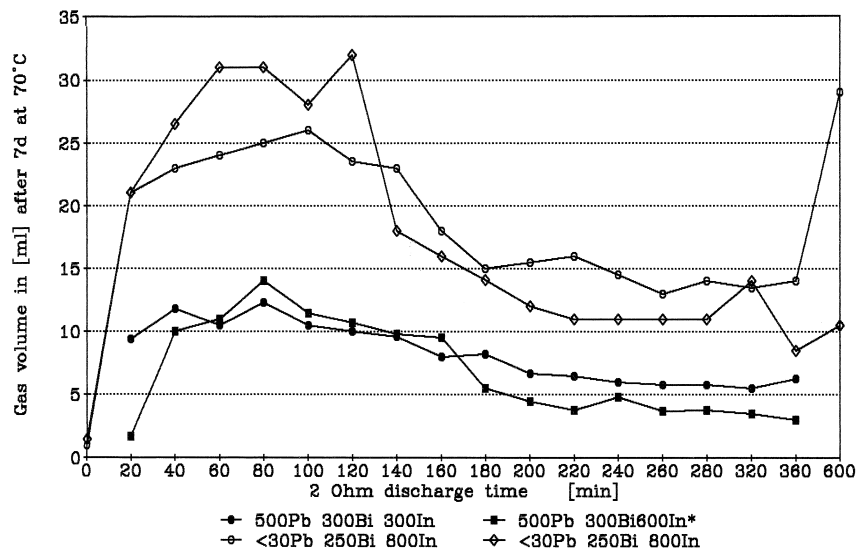


Fig. 6. Total gas evolution against time-into-discharge from four LR14 cells containing differing quantities of anode additives. One cell (*) contained 300 ppm of In in the anode, plus 300 ppm of indium oxide in the gel.

are added in the form of indium oxide show that the influence of indium in the alloy is much stronger than the influence of indium in the gel.

So far it has been shown that gas evolution as a function of discharge time can have a very strong relative maximum early in the discharge. Quite obviously this is of fundamental importance for cell manufacture and quality control of zinc powder, as the relative maximum can well be up to three times higher than the gas evolution found after longer discharge times. This means that the performance of zinc powder in alkaline cells be characterized by determining the gas evolution at relatively long discharge times. In particular, it means that it is insufficient to

qualify a zinc powder for cell manufacture just from its gas evolution in a LR14 cell after a 2 Ω , 270 min discharge, and a storage time of 7 days at 70°C, as is often done.

On the other hand it appeared to be necessary to investigate the zinc powder production method in order to find ways of reducing the maximum amount of gas evolution as a function of discharge time. Grillo have studied the zinc powder production process and as a result come up with a new production technique which lead to the zinc powder type 'UG'.

Fig. 7 gives the plot of gas evolution as a function of discharge time for conventional zinc powder of the alloy

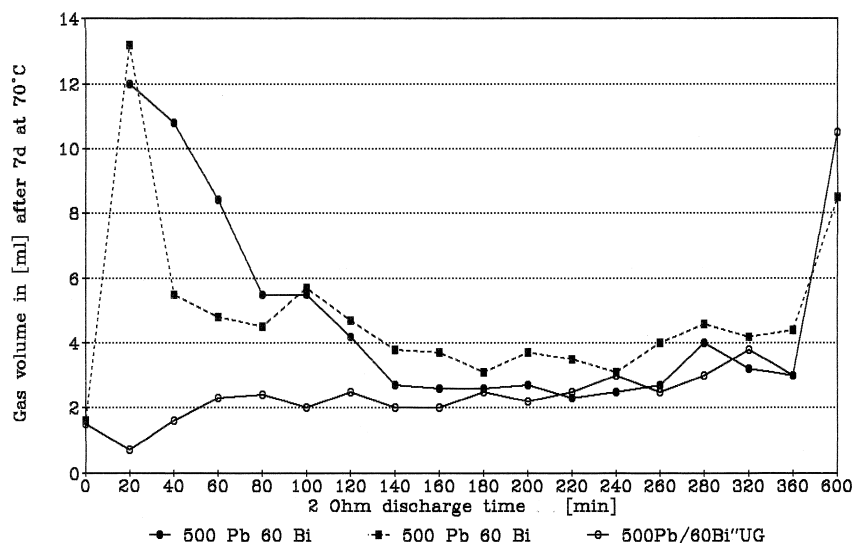


Fig. 7. Total gas evolution against time-into-discharge from three LR14 cells. The anode composition was: Zn + 500 ppm Pb + 60 ppm Bi. Two cells used conventional zinc, the third had the 'UG' type.

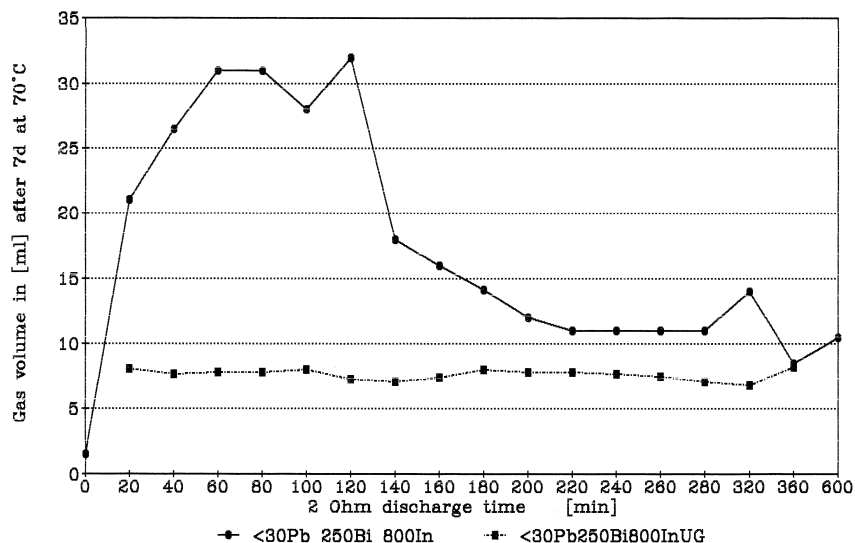


Fig. 8. Total gas evolution against time-into-discharge from two LR14 cells. The anode composition was: Zn + < 30 ppm Pb + 250 ppm Bi + 800 ppm In. One cell used conventional zinc, the other had the 'UG' type.

composition: Zn; 500 ppm Pb:60 ppm Bi: in comparison with the new zinc powder type 'UG' when used in the same alloy composition. As the figure, demonstrates, the type 'UG' does not exhibit a maximum for short discharge times.

Fig. 8 gives the plot of gas evolution as a function of discharge time for a conventional zinc powder alloy Zn; < 30 ppm Pb:250 ppm Bi:800 ppm In: in comparison with the same alloy but using Grillo type 'UG' zinc powder. The improvement in gas evolution performance of the type Grillo 'UG' is quite apparent.

4. Summary

The rate of gas evolution zinc powder in an alkaline cell depends on discharge time. The function is not propor-

tional to discharge time but may exhibit a very strong relative maximum at short discharge times, i.e., early into the discharge. This type of behaviour was found for different alloys. Grillo have investigated means to improve the zinc powder production process and have developed the modification abbreviated 'UG' from which different alloys can be produced which do not exhibit a strong relative maximum at short discharge times and has overall less gas evolution than conventional zinc powder alloys.

This process improves in particular those zinc powder alloys containing no lead but just indium and bismuth, which so far have suffered from higher gas evolution than lead-free zinc alloyed with aluminium. This meant that the BI alloys were disfavoured compared to BIC or ABI alloys, although the BI alloys do not show the problems of short circuiting at intermittent discharge as the BIC or ABI alloys do.