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Synthetic silver oxide and mercury-free zinc electrodes for silver–zinc reserve batteries

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Abstract

Reserve activated silver oxide–zinc cells were constructed with synthetic silver oxide (Ag_2O) electrodes with Pb-treated zinc electrodes produced by a non-electrolytic process. The cells were tested before and after thermally accelerated aging. At discharge rates up to 80 mA cm^{-2}, the discharge was limited by the Ag_2O electrode, with a coulombic efficiency between 89–99%. At higher rates, the cells are apparently zinc-limited. Test cells were artificially aged at 90°C for 19 h and discharged at 21°C at 80 mA cm^{-2}. No capacity loss was measured, but a delayed activation rise time was noted (192 ms fresh vs. 567 ms aged). The delay is thought to be caused by zinc passivation due to the outgassing of cell materials. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Zinc–silver oxide batteries are widely used in military applications which require tight voltage regulation as well as high energy and power density. For many of the military applications, the batteries must provide nearly instant high power, even after storage for several years at high ambient temperatures.

The storage requirement cannot be met with active primary or secondary batteries, due to the corrosion of the zinc electrode, the solubility of the silver oxide electrode, and other degradation reactions involving the separator and the electrolyte. To meet the requirement, the automatically activated reserve battery was developed at several laboratories, whereby the zinc–silver oxide cells are assembled into a battery in which the cells are kept in a dry state during the storage period until the batteries are required to operate. At which time, the electrolyte is rapidly injected into the dry battery, allowing it to deliver high power.

Modern zinc–silver oxide reserve batteries must be capable of operating at high rates of discharge (minutes) and often they must reach full power in fractions of a second after they are activated. Highly active electrodes (both silver oxide and zinc), as well as porous separators which have low hydraulic resistances are needed to fulfil the requirements.

Generally, the automatically activated reserve battery is a rugged mechanical package containing the dry cells, a hermetically sealed reservoir to contain the electrolyte, and a source of energy to force the electrolyte into the cells. Pyrotechnic gas generators are most often used for this purpose.

Cells are normally made with sintered silver cathodes [3], which are oxidized electrolytically, resulting in a random mixture of valence states (Ag, Ag_2O, and AgO) [1]. The most prevalent type of zinc anode for high rate reserve cells is the electrodeposited type, which is made by electroplating zinc from a zincate electrolyte onto a current collecting substrate. The electrodes are amalgamated with mercury to minimize the hydrogen producing corrosion reaction between zinc and water.

Zinc–silver oxide reserve batteries are, however, sensitive to age-related phenomena which most typically affect the capacity, activation time and pulse-mode voltage regulation. The capacity loss due to the thermal instability of AgO has been covered by several authors [1,2,6]. The minimum capacity requirements are normally met by including a large excess of oxidized silver as the positive active material, but the capacity changes with age, making performance prediction inexact and costly. Adding com-

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plexity to the problem is the issue of anode limitation at higher rates and lower temperatures.

The most common cause for coincident delayed activation and pulse voltage problems is a passivation of the highly reactive zinc surface of the anodes, which can result from several sources of oxygen, CO_2, or other reactive gasses or vapours within the confines of the cell space. A major source of oxygen is the decomposition of AgO within the cathodes in the closed cell space, the evolved oxygen reacting directly with the zinc:

$$2AgO = Ag_2O + \tfrac{1}{2}O_2$$

then:

$$\tfrac{1}{2}O_2 + Zn = ZnO$$

or:

$$Zn + H_2O + \tfrac{1}{2}O_2 = Zn(OH)_2.$$

The subject of this paper is reserve cells, which have cathodes made of chemically prepared Ag_2O rather than the mixed-valence-state sintered electrodes. The oxygen evolution (and capacity reducing) reaction from decomposing AgO is avoided by using the stable monovalent oxide. Also, the solid state reverse disproportionation (SSRD) reaction is avoided, a reaction which results in capacity loss but no gas evolution. The discharge performance of the chemically prepared Ag_2O electrodes in flooded half-cell tests has been reported previously [4].

This paper discusses the performance of full size automatically activated reserve cells which use the synthetic silver oxide electrodes and developmental, proprietary, zinc electrodes which contain lead as a mercury substitute. The zinc electrodes are made by a low cost, non-electrolytic, process.

2. Reserve cell tests

The test conditions were chosen which stress the cells enough to establish their capability to meet modern requirements of very rapid activation, tight voltage regulation, and efficient utilization of electrode active material. A load profile was used which included two long duration (1.00 s), very high current (300 and 400 mA cm^{-2}) pulses and baseline steady state loads of 30, 80, 120, and 200 mA cm^{-2}. Two temperature variables were included (7 and 40°C). The low temperature is a particularly difficult requirement for a zinc–silver oxide battery unaided by a heater.

3. Description of the cells

The cells were constructed with one cathode (Ag_2O) and two anodes (zinc with lead additive). The working geometric surface area of the cathode was 51 cm^2. The electrodes were made by applying a mixture of chemically prepared Ag_2O powder (from Ames Goldsmith, Glens Falls, NY, USA) and polytetrafluoroethylene (PTFE) resin as binder. An expanded metal silver current collector was used. The thickness of the finished cathodes was 0.203 ± 0.025 mm.

The zinc electrodes contained a small amount of lead as a replacement for mercury. The treated zinc was applied to an expanded silver metal current collector by a proprietary non-electrolytic process. The electrodes were 0.178 ± 0.025 mm in thickness.

The cathodes were wrapped in a single layer of porous separator. The total nominal thickness of the cell internal space was 1.22 mm. The electrolyte used was 6.3 M (28 w/w%) KOH with no additives.

4. Test results for freshly made cells

The cells with lead-treated zinc electrodes were tested at each current density and temperature variable, for a total of 19 tests. Each of the cells was activated by applying nitrogen gas pressure to a reservoir containing the electrolyte. The activation pressure was 411 kPa for all of the tests. The cells were subjected to the prescribed loads until the cell voltage dropped to 1.000. In Table 1, the coulom-

Table 1
Utilisation and average voltages of Ag_2O electrodes at various current densities

Current density (mA cm^{-2})	Temperature (°C)	Rise time (ms)	Average voltage (V)	Utilisation (%)
30	7	141.5 ± 9.19	1.416 ± 0.025	94.132 ± 8.868
80	7	160.0 ± 16.97	1.315 ± 0.007	89.178 ± 4.398
120	7	151.0 ± 0.00	1.245 ± 0.007	81.478 ± 1.886
200	7	251.0 ± 42.01	1.170 ± 0.042	41.657 ± 1.460
30	40	117.0 ± 5.65	1.410 ± 0.017	98.978 ± 0.658
80	40	111.0 ± 14.66	1.360 ± 0.00	92.396 ± 6.614
120	40	133.5 ± 7.78	1.280 ± 0.016	76.174 ± 9.256
200	40	177.5 ± 55.86	1.180 ± 0.071	56.535 ± 3.235

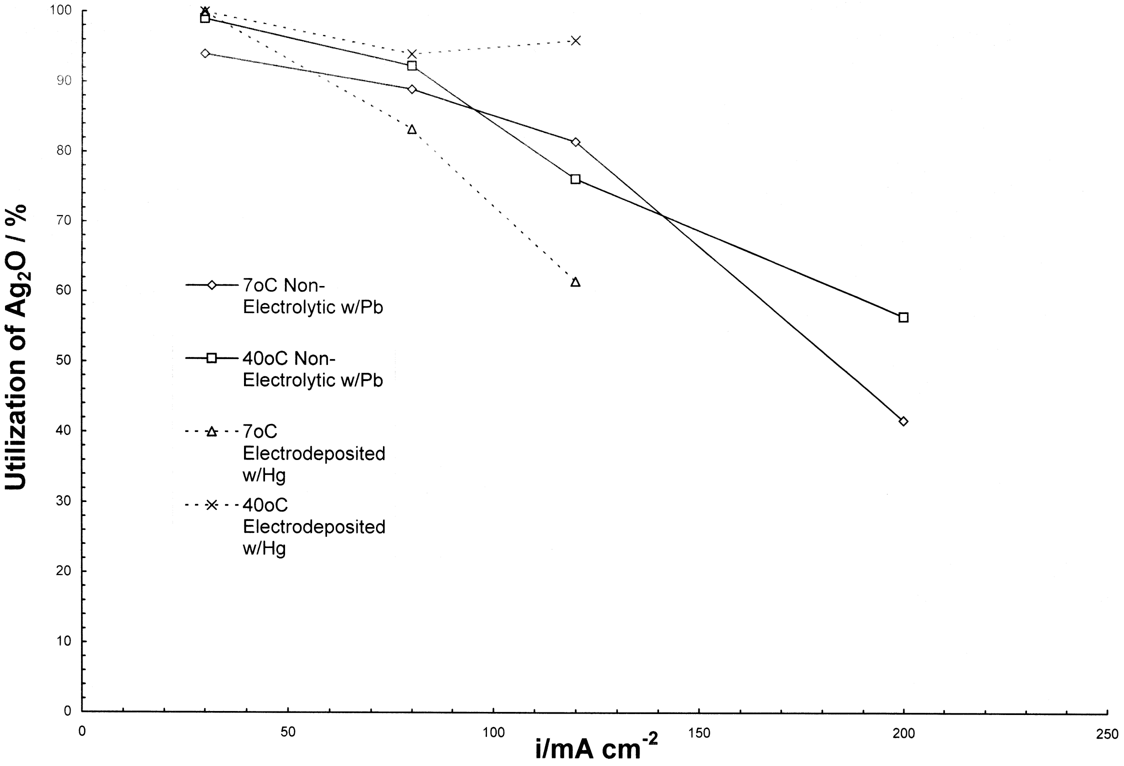

Fig. 1. Utilisation of silver oxide against current density in cells using anodes of non-electrolytic zinc containing lead or electrodeposited zinc containing mercury.

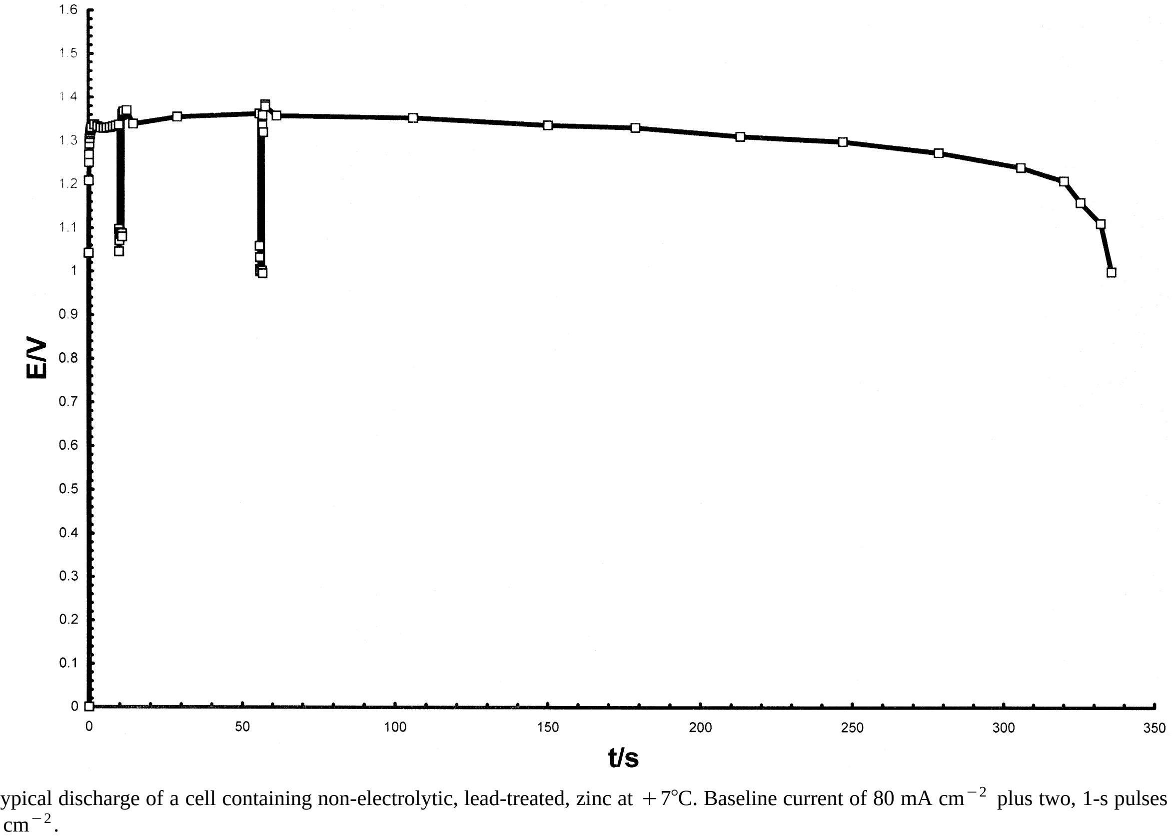

Fig. 2. Typical discharge of a cell containing non-electrolytic, lead-treated, zinc at +7°C. Baseline current of 80 mA cm^{-2} plus two, 1-s pulses at 300 and 400 mA cm^{-2}.

Table 2
Performance of two types of zinc electrode before and after aging

Electrode type	Aging regime	Rise time (ms)	Discharge time (s)	Average voltage (V)	Utilisation of Ag_2O (%)
non-electrolytic with lead	none	192	501	1.37	92.02
non-electrolytic with lead	90°C for 19 h	567	520	1.37	92.59
electrodeposited with mercury	none	129	442	1.37	82.40
electrodeposited with mercury	90°C for 19 h	377	468	1.39	76.64

bic efficiency (utilization) is expressed as a percent, based upon the actual weight of Ag_2O for each test cell.

Fig. 1 shows the utilization data for the cells using lead-treated zinc electrodes compared to cells built with commercially produced zinc electrodes which contain mercury. The amalgamated electrodes were supplied by Whittaker Power Sources Division, Denver, CO, USA). At low temperature (7°C), the cell utilization for cells built with the lead treated zinc electrodes compares favorably with identical cells made with the electrodeposited zinc electrodes with 1% Hg. However, for the cells which were tested, the electrodeposited electrodes have better utilization at higher temperature (40°C).

Fig. 2 shows a typical test for a cell with the non-electrolytic lead-treated zinc electrodes at low temperature (7°C) at a baseline current density of 80 mA cm^{-2}, with the two, 1-s pulses at 300 and 400 mA cm^{-2}, respectively. The utilization of Ag_2O was 94.084% of the theoretical value. The average voltage was 1.35, to a cut-off voltage of 1.00 V.

The activation rise time to 1.000 V was 148 ms. The first pulse (300 mA cm^{-2} for 1.000 s) was applied 10.000 s after the time zero initiation signal. The second (400 mA cm^{-2}) pulse was applied 55.00 s after the initiation signal. The minimum voltage during the 300 mA cm^{-2} pulse was 1.029 V, the minimum voltage during the 400 mA cm^{-2} pulse was 0.986 V.

5. Tests of artificially aged cells

From earlier work with Ag_2O electrode half cells, it was established that thermally accelerated aging has no affect upon the performance of the silver oxide (Ag_2O) electrodes [5]. Tests of full size reserve cells were performed in this work to characterize the effects of aging upon the complete cell, with zinc electrodes, separator, cell case, and adhesives.

The test cells were constructed with the components as previously described. The only variable for the aging tests

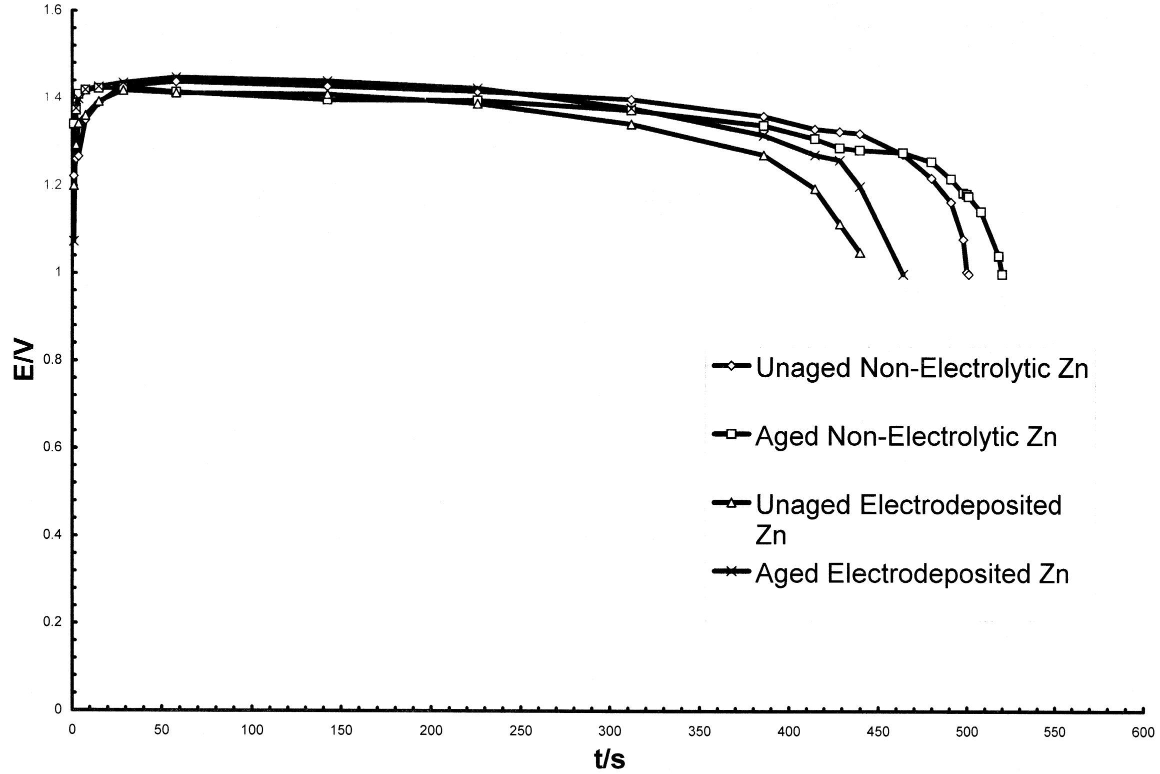

Fig. 3. Discharge performances of fresh and aged cells. Discharged at 80 mA cm^{-2}.

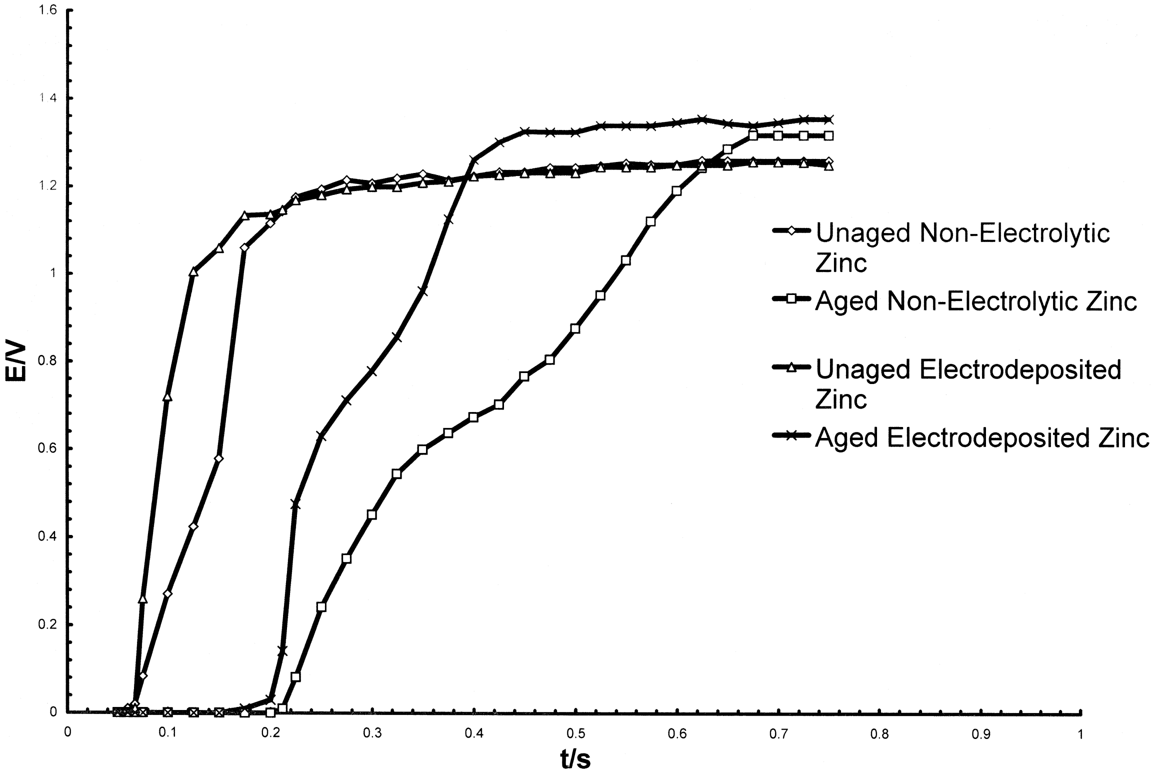

Fig. 4. Activation characteristics of fresh and aged cells. Discharged at 80 mA cm^{-2}.

was the zinc electrodes which were used: the non-electrolytic zinc electrodes with lead additive and electrodeposited zinc (with 1% Hg) electrodes.

The cells were artificially aged by subjecting them to 90°C for 19 h. The cells were stored in sealed metal paint cans after they had been evacuated and backfilled with dry nitrogen. The intent of the tests was to determine how the cells with non-electrolytic zinc electrodes performed in comparison with the cells using the industry-standard zinc electrodes.

After the storage period, the cells were activated at 21°C with 6.3 M (28 w/w% KOH). The activation pressure was 411 kPa. The cells were activated into a constant load of 80 mA cm^{-2}. The results are summarized in Table 2.

The V/t curves for the entire discharges are presented in Fig. 3. The activation rise times are shown in Fig. 4. The thermally accelerated aging environment has no significant affect upon the capacity of the cells. However, the utilization (based upon the amount Ag_2O present) is better for the cells with non-electrolytic zinc electrodes than for the cells with amalgamated electrodeposited zinc electrodes.

The activation performance of the cells is, however, affected by the high temperature storage, even with an Ag_2O electrode which does not evolve oxygen. Of interest is the fact that the onset of voltage is nearly identical for both types of electrodes for the two artificial aging conditions, but the slopes of the V/t curves are different.

The cause for the delayed activation will be the focus of future planned work. The outgassing of the cell materials is believed to contribute where the vapours can be expected to react with the active zinc surface, leaving a passivating film.

6. Conclusions and observations

These low cost synthetic silver oxide and lead-treated zinc electrodes are capable of very rapid activation and excellent voltage regulation at high rates of discharge and during high-power pulse loads at low temperature.

At discharge rates less than 80 mA cm^{-2}, the cells are cathode limited, and the cathode discharge efficiency is the same (92–94%) as determined during the flooded half cell tests previously reported. However, at rates in excess of 80 mA cm^{-2}, the cells appear to be anode limited.

There is no capacity loss resulting from storage of the cells at high temperature (90°C). There is, however, an increase in the activation time delay of cells after they are artificially aged. Both electrodeposited zinc electrodes with mercury and the non-electrolytically produced electrodes with lead are affected. The cause is thought to be related to the reactive nature of the zinc electrode in the dry state and the outgassing of the materials of construction of the cells.

Further work will be reported in the areas of gas evolution rate measurement and aging affects on the cells.

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