

Aging in chemically prepared divalent silver oxide electrodes for silver/zinc reserve batteries

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Abstract

The instability of silver(II) oxide electrodes used in silver/zinc reserve batteries is the well known cause of capacity loss and delayed activation in reserve batteries after they are stored in the dry, unactivated state for extended periods of time. Metal contaminants in sintered/electroformed electrodes destabilize the oxide and the solid state reaction between AgO and elemental silver results in the formation of the lower capacity monovalent oxide Ag₂O. Chemically prepared (CP) AgO can be used to avoid the metal contaminants and to minimize the interfacial contact area between AgO and Ag, thus minimizing the affects of aging on the electrodes.

Electrodes were fabricated with CP AgO and polytetrafluoroethylene (PTFE) binder and expanded silver metal current collectors. Experimentally, both electrode active material compacts (AgO and binder only) and electrodes complete with AgO/binder and silver current collector were tested to evaluate the influence of the current collector on aging. The electrode samples were discharged at a constant rate of 50 mA cm⁻² before and after storage at 60°C for 21 days as well as after storage at room ambient temperature conditions for 91 months.

The results indicate that the affects of aging upon the AgO/binder compacts are insignificant for long term storage at room temperature. However, thermally accelerated aging at high temperature (60°C) affects both transient and stabilized load voltage as well as capacity. In terms of capacity, the AgO/binder mix itself loses about 5% capacity after 21 days dry storage at 60°C while electrodes complete with current collector lose about 8%. The 60% increase in capacity loss is attributed to the solid state reaction between AgO and elemental silver. © 2001 Elsevier Science B.V. All rights reserved.

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1. Background

Silver/zinc reserve batteries are used in missiles and other military applications primarily because of their very high power density. The batteries can be stored in their dry, unactivated state for several years until they are called upon for operation. The batteries are activated by manually or automatically injecting the electrolyte (typically KOH solution) into the cells.

The battery voltage and capacity tend to decrease as the batteries age during the dry, unactivated storage period. A major cause for the decline in performance of silver/zinc reserve batteries is the instability of the silver electrode. To date, most silver/zinc batteries are produced with sintered silver electrodes which have been anodized in KOH solution to produce silver oxide. Typically, the electroformed electrodes contain a mixture of Ag, AgO, and Ag₂O along with

Ag₂CO₃ and residual H₂O, KOH, K₂CO₃ from the charging process. The higher oxide commonly referred to as AgO has been established to be Ag₂O₃·Ag₂O [1].

Particular attention has been focused on the higher oxide AgO, which has nearly twice the capacity of the monovalent oxide (0.43 Ah g⁻¹ for AgO versus 0.23 Ah g⁻¹ for Ag₂O). However, the AgO is thermodynamically unstable. Dallek et al. have reported a broad range for the activation energy of decomposition (E_a) from 100 kJ mol⁻¹ to as high as 133 kJ mol⁻¹ [2]. The lowest E_a was from electroformed electrodes while chemically prepared AgO had the highest activation energy. Contaminant metals such as Cu can be introduced as part of the electroformation process and have been shown to significantly destabilize the AgO [3].

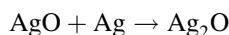
2. Chemically prepared silver oxide electrodes

In previous work, silver oxide (both AgO and Ag₂O) electrodes were studied which were based upon the use of

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chemically prepared oxides [4]. The AgO was prepared by persulfate oxidation of AgNO₃ and the Ag₂O was prepared by precipitation of AgNO₃ solution with alkali. The stability of such electrodes is believed to be greater than electroformed electrodes for several reasons.

Electroformed electrodes include a dispersed phase of elemental silver particles because of incomplete conversion. The relatively high surface area of the interface between AgO and the Ag particles leads to the loss of AgO by the solid state reaction:



The destabilizing metal contaminants are completely absent in the chemical oxide electrodes, which contain only trace amounts of Ni, and Cu. Also absent are the residual water and carbonates which can also affect the stability of the AgO.

The most stable electrode is obviously made with the stable oxide Ag₂O, which has a decomposition temperature of nearly 700 K. However, the higher capacity of AgO may be required in a limited number of applications.

The subject of this paper is the electrical characterization of electrodes produced with chemically prepared AgO as a function of age.

3. Experimental method

Chemically prepared AgO was obtained from Ames Goldsmith Company, Glens Falls, NY, USA. The oxide was produced by persulfate oxidation of AgNO₃ solution.

The AgO was blended with PTFE binder. No additives to increase the conductivity of the electrode active mass were used. Samples of the compacted AgO binder were stored for 91 months at room ambient temperature. Subsequent tests were performed to characterize the affects of the long term storage under benign conditions and after storage at elevated temperature.

4. Capacity after storage at 100°C

A baseline group of electrodes was prepared “fresh” before the AgO/binder compacts were stored for the 91 months period. The nominal thickness was 0.35 mm and the loading of AgO/binder mix was 120–140 mg cm⁻². The test samples were then discharged in an excess of 6.3 M KOH solution at room ambient temperature against a nickel foam counterelectrode. The electrodes were discharged after various periods of dry oven storage at 100 ± 1°C. The voltage was measured against an amalgamated zinc reference electrode and the capacity was determined to a cutoff voltage of 1.00 V at the discharge current density of 80 mA cm⁻². Corrected for the amount of binder and the assay amount as AgO and Ag₂O, the utilization without storage at high temperature was 94.90% of the theoretical value.

Table 1

Utilization of oxides before and after storage at 100°C

Storage time at 100°C (h)	Utilization (to 1.00 V versus Zn(Hg) reference) (%)
Fresh, no storage	94.90
42.5	70.45
95.0	53.34
168.0	43.11
250.0	44.71

The remaining electrodes were removed from the storage oven after various periods of time, then discharged as described above.

The results are presented in Table 1 and in Fig. 1.

5. Real time aging of the AgO/binder mix before electrode fabrication

Compacted portions of the blend of AgO and PTFE were stored at uncontrolled room ambient temperature condition for 91 months. The compacts were then pressed onto silver expanded metal current collecting grids. The thickness and loading of the resulting electrodes was nominally 0.15 mm (50 mg cm⁻²) and 0.30 mm (125 mg cm⁻²).

The discharge tests characterize the affects of the long term (years) room temperature aging and the PTFE binder on the stability of the AgO. The electrodes were discharged in excess 6.3 M KOH at 20–21°C, at a current density of 50 mA cm⁻². A machined acrylic test fixture was used which positioned a foam nickel counterelectrode, a separator (Celgard 3401), the working electrode, and an amalgamated zinc reference in a reproducible manner. Accordingly, the electrode was discharged from one face only, with the reaction zone being up to 0.30 mm in depth. The reference electrode was located 3 mm behind the centrepoint of the working electrode.

An EG&G Model 362 Scanning Potentiostat was used to discharge the test cells. The voltage of the working electrode (versus reference) was recorded with a 16 bits PC-based data acquisition system.

The capacity of the AgO electrode was calculated from the time to reach a cutoff voltage of 1.000 V versus reference. The utilization in terms of percentage of the theoretical value was corrected for the amount of inert binder, and the percent AgO and Ag₂O in the original sample. The correction for the amount of binder assumed perfect dispersion of the PTFE. The data is presented in Table 2

The results are in rough agreement with the calculated decomposition rate predicted by Dallek [5] who calculated a minimal 0.4% conversion of CP AgO to Ag₂O in a 101 months storage period at 25°C.

Given the experimental error in our tests, no measurable decrease in capacity was observed after the actual long term aging for the AgO–PTFE mix itself, indicating that the PTFE and the process itself had no significant destabilizing affect upon the AgO.

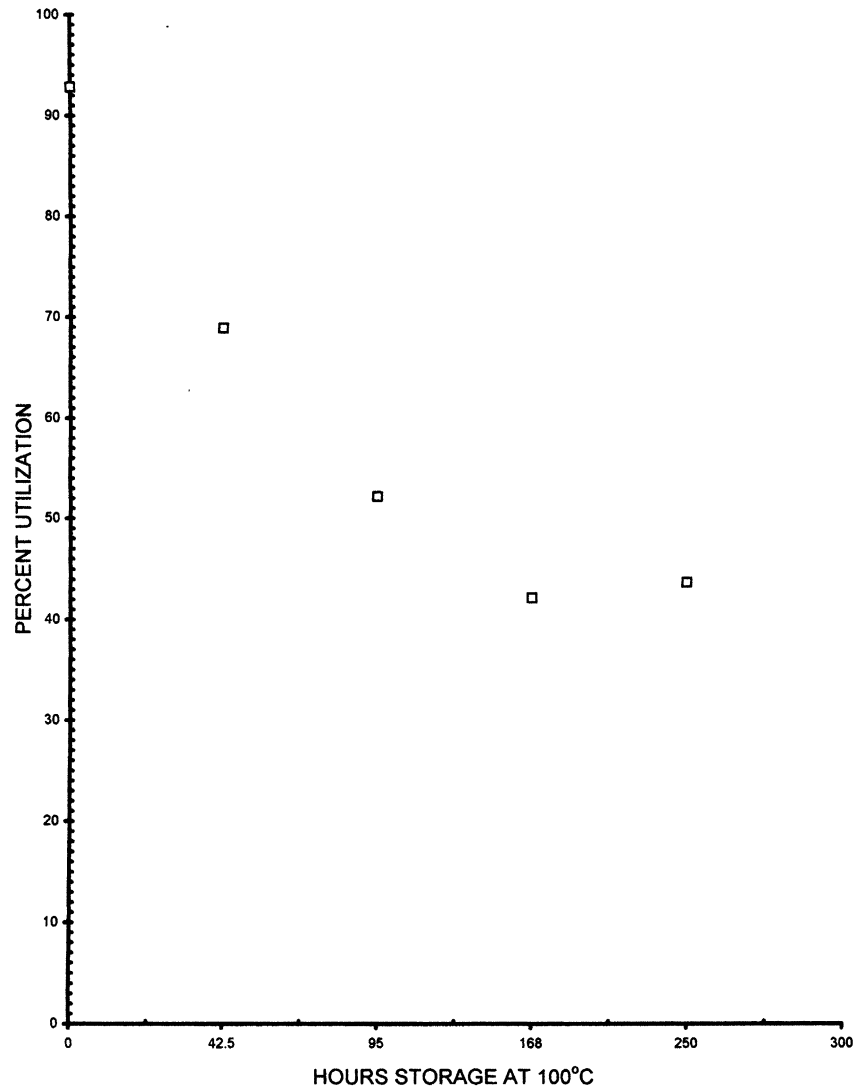


Fig. 1. Utilization of oxides before and after storage at 100°C.

6. Accelerated aging of the AgO/binder mix before electrode fabrication

One of the many thermally accelerated aging test methods is to subject batteries to oven storage at 60°C (333 K) for 21 days. Using the predictive model of Dallek [5], only 0.64%

Table 2
Utilization of the AgO/binder mix to 1 V versus zinc reference electrode after storage for 91 months at room temperature

Test electrode number	Thickness (mm)	Utilization (%)	Average voltage (V) (versus Zn(Hg) reference)
1	0.15	97.77	1.54
2	0.30	100.99	1.55
3	0.30	101.84	1.56
4	0.30	100.28	1.55
5	0.30	100.19	1.57
6	0.30	100.11	1.56

of the CP AgO is predicted to decompose after the 21 days dry storage at 60°C (0.34% capacity loss).

The electrodes were prepared in an identical manner as described in clause 3. In this case, however, the AgO/binder compacts (no current collector) were heated at $60 \pm 1^\circ\text{C}$ for 21 days in a mechanically convected oven. After heat treatment, the AgO/binder mix was then applied to silver expanded metal current collectors. The electrodes were then discharged in half cells under the same conditions as previously described, at a current density of 50 mA cm^{-2} .

The results are presented in Table 3

On average, the 60°C storage for 21 days resulted in a loss in capacity of about 5.6% rather than the predicted 0.34% loss. In addition to the loss in capacity, a degradation in voltage was noted. The initial open circuit potential (OCP), the initial load voltage at 50 mA cm^{-2} , and the stabilization voltage at 1 s is summarized in Table 4, comparing room temperature aging (91 months) and high temperature aging (60°C for 21 days).

Table 3

Utilization of the AgO/binder mix to 1 V versus zinc reference electrode after storage for 21 days at 60°C

Test electrode number	Thickness (mm)	Utilization (%)	Average voltage (V) (versus Zn(Hg) reference)
7	0.30	95.78	1.50
8	0.30	92.97	1.55
9	0.30	94.34	1.52
10	0.30	94.83	1.50
11	0.29	94.02	1.47

As indicated in Table 4, the open circuit potential for room temperature aged AgO/binder electrodes was not reproducible and was somewhat less than expected. The deviation from the AgO/Ag₂O potential is assumed to be the result of the 91 months room temperature storage of the AgO/binder. However, after storage at 60°C for 21 days, the OCP approached that of the Ag₂O/Ag vs Zn.

It is assumed that the decomposition of AgO to Ag₂O and/or the formation of Ag₂CO₃ are surface phenomena, and when the mix compact was applied to the silver current collector (after thermal treatment) the Ag₂O and/or Ag₂CO₃ interface with the Ag is the cause of the depressed voltage.

7. Thermally accelerated aging with a silver grid in contact with the mix

Tests were performed to determine the affect of the solid state reaction between AgO active material and the silver metal current collector:



Electrodes were fabricated by applying the AgO/binder compact to silver current collectors, using the identical process described above. In this case, however, the complete electrodes with Ag current collector in place were heated at

Table 5

Utilization of electrodes to 1 V versus zinc reference electrode after storage for 21 days at 60°C

Test electrode	Thickness (mm)	Utilization (%)	Average voltage (V) (versus Zn(Hg) reference)
A	0.30	96.37	1.49
B	0.30	88.53	1.47
C	0.30	89.85	1.51
D	0.30	93.45	1.53
E	0.30	94.32	1.52
F	0.30	93.84	1.52
G	0.30	90.84	1.53

60°C for 21 days in a mechanically convected oven. The electrodes were then discharged in flooded half cells at the same current density (50 mA cm⁻²).

The capacity and average load voltage of the test electrodes is summarized in Table 5.

Fig. 2 shows the typical performance at 20°C, 50 mA cm⁻² current density, for a CPAgO electrode. Electrode A is shown.

The apparent affect of the current collector during storage at 60°C for 21 days is a greater reduction in capacity (on average about 7.5 versus 5.6% for the previous tests of AgO/binder without the current collector). The capacity loss is a significant deviation from the predicted 0.64% decomposition for CPAgO alone. The apparent difference is caused by the solid state reaction of the Ag grid with the AgO.

The data, however, indicates an increased stability over the typical for sintered and electroformed silver electrodes. Bagshaw and Brown [6] observed a 23.9% capacity loss after 1 month storage at 60°C, while Bowers and Gubner [7] found a reduced capacity loss of about 10% after 1 month at 54°C. The variability of the sintered electrodes is presumably caused by the influence of the grid, the unconverted silver phase, and the destabilizing contaminants which are associated with the electroformed electrodes.

Table 4

Comparison of electrode performances following room and 60°C storage of the constituent mix

Test electrode/aging temperature	Open circuit voltage (versus Zn(Hg) reference) (V)	Voltage at 100 ms (versus Zn(Hg) reference) (V)	Voltage at 1 s (versus Zn(Hg) reference) (V)
1 (Room)	1.7370	1.5317	1.5824
2 (Room)	1.8497	1.4900	1.5655
3 (Room)	1.7620	1.4952	1.5928
4 (Room)	1.6728	1.5055	1.5502
5 (Room)	1.7130	1.5502	1.5876
6 (Room)	1.6895	1.5340	1.5583
Average ± 1 S.D.	1.737 ± 0.064	1.517 ± 0.024	1.573 ± 0.017
7 (60°C)	1.6604	1.4422	1.4742
8 (60°C)	1.6950	1.5249	1.5515
9 (60°C)	1.6759	1.3824	1.4146
10 (60°C)	1.6725	1.5019	1.4782
11 (60°C)	1.6786	1.1632	1.3384
Average ± 1 S.D.	1.676 ± 0.012	1.403 ± 0.145	1.451 ± 0.079

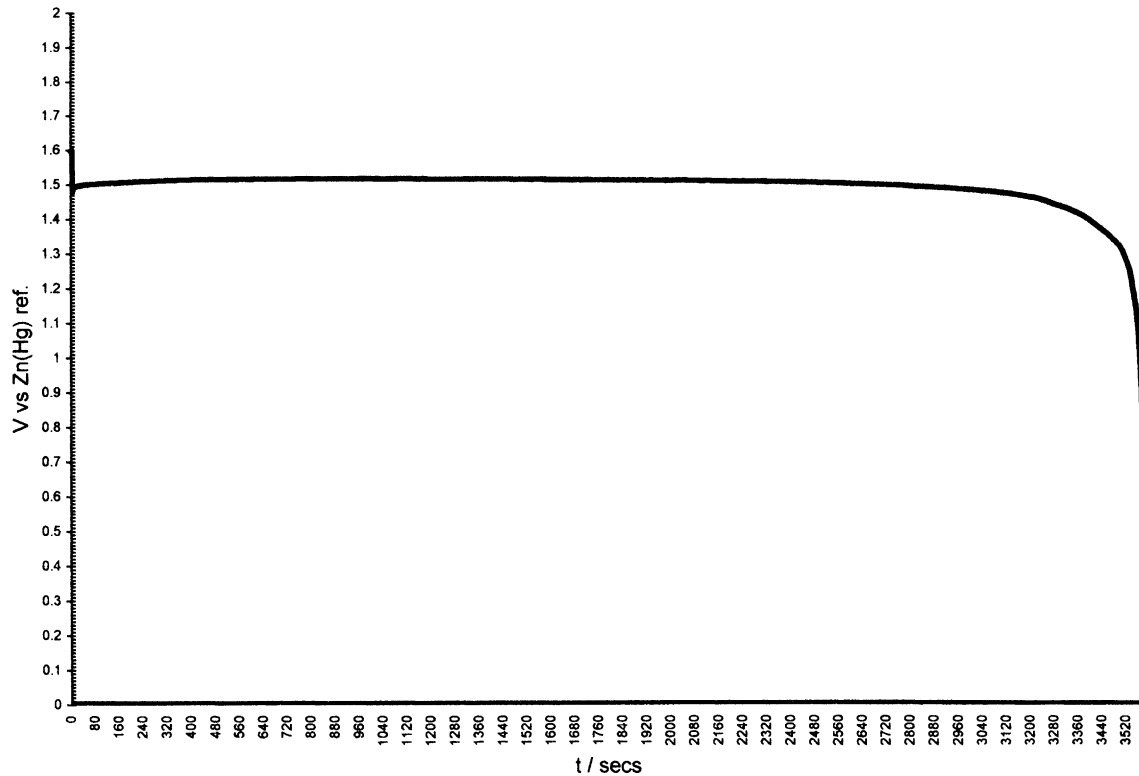


Fig. 2. Typical 20°C performance of chemically prepared AgO (electrode A) at 50 mA cm⁻².

The initial OCP, the initial load voltage at 50 mA cm⁻² and the stabilization voltage for the thermally aged complete electrodes is summarized in Table 6.

As indicated in Tables 5 and 6, the open circuit potential has approached that of the Ag₂O/Ag electrode. In this case, the Ag₂O at the active material/grid interface is probably the Ag₂O reaction product from the solid state reaction with the grid itself.

Of note is the data in Table 6, which shows much improved transient performance for the aged samples, which included the grid during the thermal treatment. It appears that the grid interface is much more uniform for this case.

Fig. 3 shows the onset of polarization of an electrode which has not been thermally aged and one which has been

subjected to dry storage at 60°C for 21 days. The tests chosen were those electrodes from the groups which exhibited the greatest voltage dip. There is scatter in the data, but the general trend of the limited number of tests is toward an increased magnitude of the voltage dip for the thermally treated samples. There is also an increased steady state polarization (by ~50 mV) resulting from the thermally accelerated aging.

8. Summary

The sintered and electroformed silver electrodes normally used are a mixed composition of Ag, Ag₂O, AgO, and

Table 6
Performance of thermally aged electrodes, following 21 days at 60°C

Test electrode	Open circuit voltage (versus Zn(Hg) reference) (V)	Voltage at 100 ms (versus Zn(Hg) reference) (V)	Voltage at 1 s (versus Zn(Hg) reference) (V)
A	1.5971	1.4773	1.4927
B	1.6244	1.4423	1.4586
C	1.6139	1.4773	1.4586
D	1.6182	1.5052	1.5162
E	1.6118	1.5575	1.5077
F	1.6233	1.5613	1.5120
G	1.6534	1.4882	1.5273
Average ± 1 S.D.	1.620 ± 0.017	1.501 ± 0.044	1.527 ± 0.022

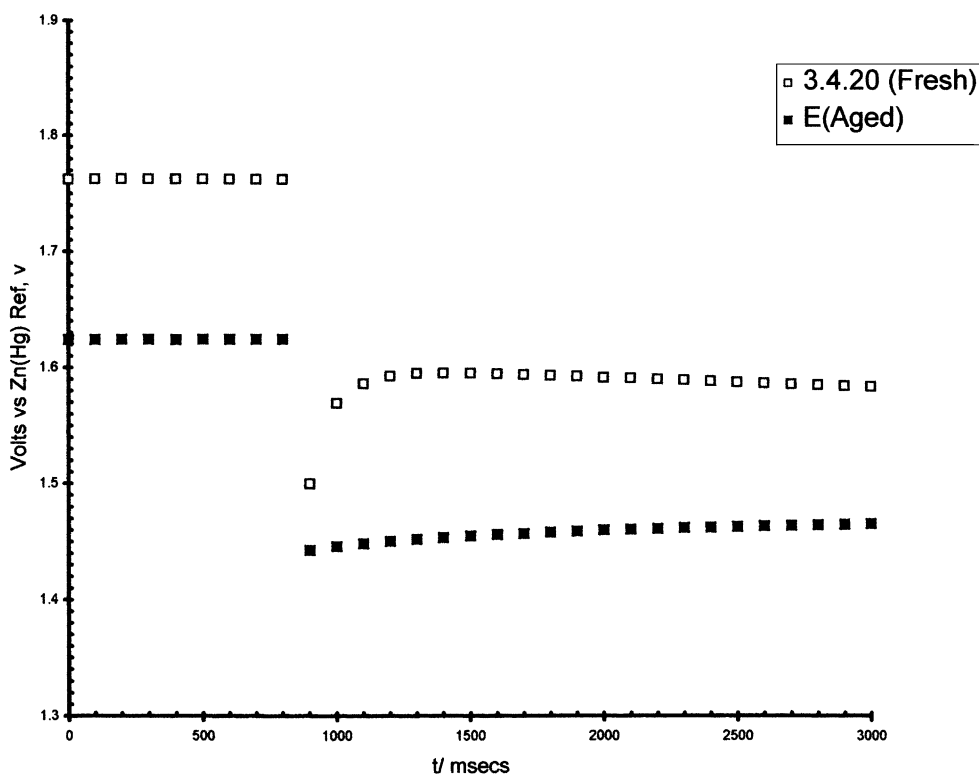


Fig. 3. Onset of polarization of an electrode which has not been thermally aged and one which has been subjected to dry storage at 60°C for 21 days.

Ag_2CO_3 . As a consequence of the random nature of the anodization process and the electrode morphology, the electrodes have a random chemical composition and morphology, which affects the performance of the electrodes, especially after aging.

Destabilizing contaminants such as Cu, residual water, and K_2CO_3 are extremely difficult to exclude from the silver oxide plates which are processed by anodization in aqueous media. Particularly, troublesome are the metallic contaminants.

Many of the aforementioned problems can be avoided by the use of chemically prepared silver oxide and a non-reacting binder such as polytetrafluoroethylene. With such electrodes, a highly ordered structure free from a dispersed phase of elemental silver will be more stable than the sintered/electroformed variety, which can have a substantial amount of unreacted silver in random locations.

The decomposition of chemically prepared AgO itself follows an Arrhenius behavior which can be predicted with reasonable accuracy. The electrochemically converted electrode active material, however, is much more difficult to model, because of the random nature of the electrodes and the existence of destabilizing contaminants.

As shown in the tests which are the subject of this paper, the predicted conversion of AgO to Ag_2O as a consequence of aging is much less than the actual experience, presumably due at least partially to the reaction of between AgO and the grid.

Of prime importance is the fact that the efficiency of discharge for the chemically prepared AgO electrodes is extremely high, and there is only a small amount of inert binder. Accordingly, the electrodes have a much higher energy density at the plate level than normal sintered and electroformed electrodes. In previous work, the energy density of this type of AgO and sintered and electroformed electrodes was determined at high discharge rate. The tests were conducted in driven cells in flooded electrolyte in similar fashion to the tests described in this work [4]. The results are summarized in Table 7.

However, in some applications which require very precise voltage regulation and rapid activation, even chemically prepared AgO can cause problems. The data indicate a decline in the reproducibility of transient voltages with load changes after accelerated aging. The oxygen evolution as a consequence of AgO instability can also cause passive films to build on zinc electrodes which is known to impair the rapid activation of some batteries.

Table 7
Comparison of the performances of chemically and sintered/electroformed AgO

Electrode type (AgO)	Average voltage (V)	Utilization (Ah g ⁻¹)	Wh g ⁻¹	Wh cm ⁻³
Chemically prepared	1.526	0.428	0.446	2.585
Sintered/electroformed	1.594	0.233	0.259	1.825

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