New developments in very high rate silver oxide electrodes

David F. Smith [a], George R. Graybill [a], Robert K. Grubbs [a], James A. Gucinski [b],*

[a] EMF Systems, Inc., Boulder Creek, CA, USA
[b] Naval Surface Warfare Center, Crane Division, Crane, IN, USA

Abstract

Cathodes for primary silver/zinc cells were prepared using chemically synthesized silver oxides (both monovalent and divalent). The oxides were mixed with PTFE binder but with no conductive fillers for this work. The electrodes were discharged galvanostatically over a broad range of current densities (40–500 mA cm^{-2}) and temperature (7–40°C) in 6.3 M KOH electrolyte. The discharge capacity was greater than 90% of the theoretical value for both oxides under such conditions. At high rate (500 mA cm^{-2}) the overvoltage of the monovalent oxide is about 50 mV less than that for the divalent oxide. A 42% improvement in energy density over anodized silver cathodes was demonstrated with the chemical AgO electrodes.

Keywords: Silver oxides; Zinc anode reserve batteries

1. Introduction

Silver/zinc primary-reserve batteries were first developed during the 1950s and 60s, for use in military applications where high energy and power density was needed. Since that time, the rapid advancement in electronics technologies has created the need for improvements in performance such as better voltage regulation coincident with longer storage life. Recently, new silver oxide [1–3] and zinc electrode structures have been developed which address the new requirements. The focus of this paper is the silver oxide electrode.

The most widely used silver oxide electrode for reserve batteries is the electroformed type. The electrodes are usually made by depositing silver powder directly onto expanded silver substrates or by pasting Ag_2O onto the substrate and subsequently decomposing the oxide mass of monovalent silver oxide (Ag_2O) to silver metal. The electrodes are then anodized to produce the oxide. The resulting electrodes are physically rugged and are capable of discharge at a high rate. However, the electroactive material is always a non-uniform mixture of monovalent and divalent oxide, and uncharged silver.

The non-uniform stoichiometry of the electroformed type of electrode and the high cost of production prompted several workers to use chemically prepared silver oxides (both AgO

and Ag_2O) as active material for new electrode designs. Wilburn [4] and Wilburn and Bradley [5] applied AgO powder directly to expanded metal substrates both with and without carboxymethyl cellulose (CMC) binder. The resulting structures were of acceptable physical strength for the handling and operation of a missile battery, but were not as rugged as the electroformed plates. The utilization of the chemical oxide plates was demonstrated to be 20–30% greater than the utilization of silver in electroformed plates at current densities up to 667 mA cm^{-2} at 46°C.

Coleman and King [6] included 1–5% graphite with chemically prepared AgO as a conductive additive. They also reported better utilization than electroformed silver electrodes at a current density of 170 mA cm^{-2} at room temperature but the electrodes exhibited about 100 mV greater overvoltage than electroformed electrodes.

Lang [7] reported on a manufacturing process for direct rolling of AgO powder without binder onto silver expanded metal substrates. The electrode performance was improved as the density increased, with a final porosity in the 30% range.

Monovalent silver oxide is presently used compounded with 1–5% graphite as a conductive additive for use in low-rate button cells (Passanti and Megahed) [1], due to the high resistivity of Ag_2O. The resistivity of the monovalent oxide is in the 10^8 ohm cm range [9].

Battery designers using divalent silver oxide must compensate for the capacity loss during long term storage of

---

* Corresponding author.

reserve batteries, caused by the thermal instability of the AgO. The decomposition proceeds by:

$$2AgO \rightarrow 2Ag + O_2 \qquad (1)$$

and by a reaction between the active material and elemental silver embedded in the electroactive structure by a solid state reverse disproportionation (SSRD) reaction:

$$AgO + Ag \rightarrow Ag_2O \qquad (2)$$

Dallek et al. [10] predicted the capacity loss of electro-formed AgO (free of destabilizing contaminants) was less than 5% for AgO stored at 40°C for 101 months. In practice, the capacity loss for actual electroformed electrodes is much greater. They suggest that the SSRD reaction (2) proceeds at a lower temperature than (1) and may account for a large part of the decomposition.

2. Approach

Ageing of silver/zinc reserve batteries, particularly as related to voltage delay upon activation, has always been a problem. Our approach was to evaluate the use of chemically prepared Ag_2O as active material rather than the less stable AgO in electrodes using a small amount of polytetrafluoro-ethylene (PTFE) as binder. The Ag_2O is thermally stable compared to AgO (the decomposition temperature is approx-

imately 420°C, while that for AgO is approximately 220°C) [8]. The use of the monovalent oxide will eliminate the evolution of oxygen from the positive electrode which occurs when batteries are stored under practical conditions. Also, the SSRD reaction will not occur. No conductive additives were used in this work.

Divalent oxide electrodes, using the chemically prepared powder, do not contain destabilizing metal contaminants. The absence of a highly dispersed elemental silver phase may mitigate somewhat the affect of the SSRD reaction in the cases where divalent oxide electrodes are used and thus improve the ageing stability of AgO electrodes.

Modern reserve battery requirements often include very tight voltage regulation while the current requirement covers a wide range, particularly for pulse-type applications. A cor-ollary requirement at the electrode level is that the highest possible rate capability be attained, to minimize the voltage drop. Accordingly, for this work, the chemical oxide elec-trodes were tested at rates from 40 to 500 mA cm^{-2}, acknowl-edging that, at very high rates, the zinc electrode will be limiting. Our approach was to optimize the rate performance of the *cathode* to minimize the polarization losses at normal rates of discharge.

3. Experimental

Chemically prepared oxides, both mono- and divalent (from Ames Goldsmith Company, Glens Falls, NY, USA),
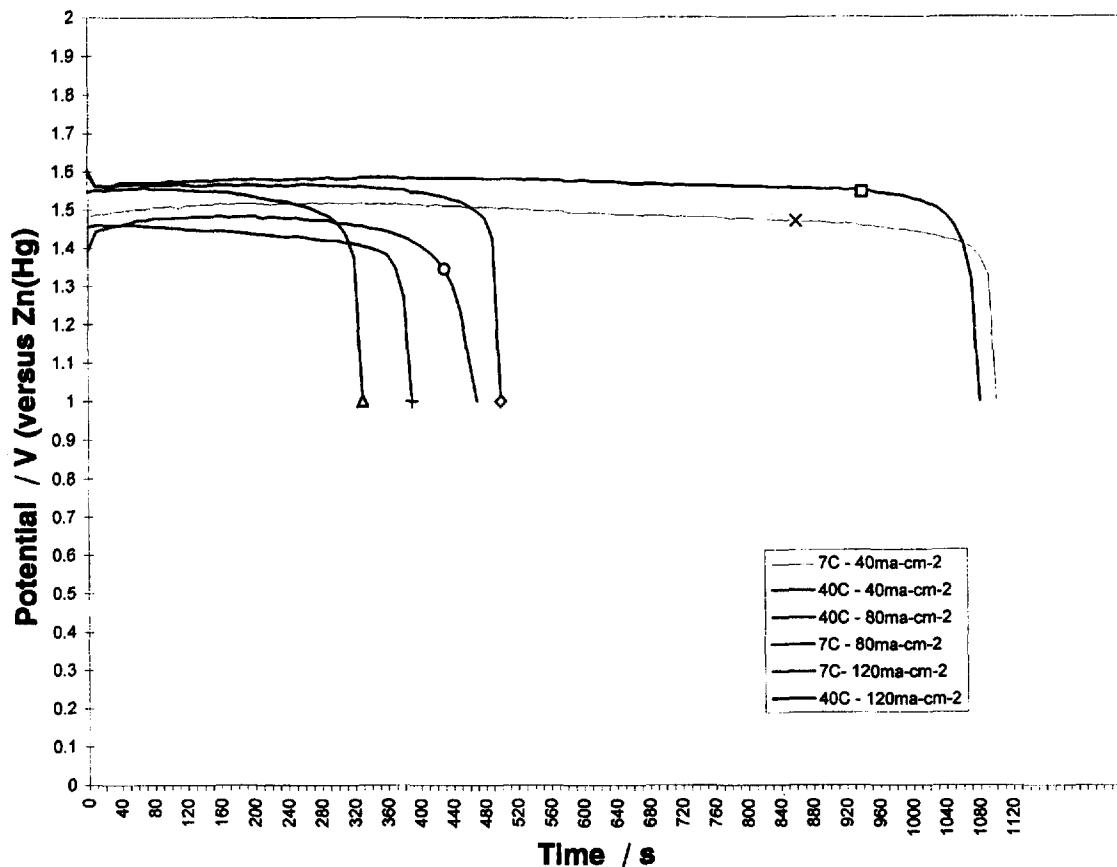

Fig. 1. Ag$_2$O electrodes discharging at moderate current densities, +7 and +40°C.

were blended with PTFE binder and applied to expanded silver current collectors by a proprietary process. No conductive fillers were used. The loading of the active material mix was nominally 3.6 g cm^{-3}. The final thickness of the electrodes was nominally 0.25 mm.

The rate capability of the chemical oxide electrodes as well as electroformed silver electrodes was characterized by galvanostatic discharge in 6.3 M KOH electrolyte. The test cell consisted of the silver oxide (working) electrode, a nickel foam counterelectrode, and a single layer of Celgard 3401 microporous polypropylene separator, used to keep the gas evolved from the counterelectrode separate from the working electrode. The reference electrode was mounted centrally behind the working electrode. The cell components were housed in a machined acrylic plastic cell body. The cell assembly was equilibrated at the discharge temperature (7 and 40°C) in a Tenney Jr. environmental chamber.

4. Galvanostatic discharges

The working electrodes were 22.8 mm × 30 mm in size. A Hewlett-Packard model 6256B power supply was used to discharge the electrodes at constant rates from 40 to 500 mA cm^{-2}. The working electrode potential was measured against a simple zinc amalgam reference electrode. The data were acquired with a PC-based data acquisition system.

Fig. 1 shows the discharge results for a series of tests performed at moderate current densities (40, 80 and 120 mA cm^{-2}) at 7 and 40°C. The temperatures chosen represent a practical operating temperature range for several missile batteries. In all cases, the electrodes were immersed in the test cell and the discharge was initiated after a 30 s no-load period.

The utilization and average voltage of the tests of Fig. 1 are presented in Table 1. The data are referred to a 1.00 V cutoff versus a zinc amalgam reference.

The average voltage at 40°C decreases monotonically as the current density increases, as expected. The 7°C voltage data, however, show an increase. The reason for these phenomena has not been determined.

5. Morphology

The reduction of Ag$_2$O to Ag in the chemically prepared oxide electrodes occurs exclusively at the grid/active material interface. Electrodes were discharged to depths of dis-

charge corresponding to 5% and 50%, based upon the theoretical values. The discharges were performed at 7°C and 80 mA cm^{-2} current density, in 6.3 M KOH electrolyte. The electrodes were rinsed thoroughly in de-ionized water, and dried at 100°C in a vacuum oven for 2 h. A coupon of each electrode sample was mounted for cross section preparation. The light optical microscope (LOM) images, taken under bright field, are included as Figs. 2–5. The sections were taken at a magnification of 154 × while the planar views are 34 × images. Fig. 6 is a planar scanning electron microscope (SEM) image taken at a magnification of 1500 ×. Fig. 7 is a similar image taken of the cross section. The large object at the center left side of the photograph is the silver metal grid.

The expanded silver metal grid is shown clearly, as is the bulk of the electrode's Ag$_2$O active material. The silver metal is light compared to the dark oxide. The photographs show conclusively that the initial reaction site is at the grid/Ag$_2$O interface, and that the discharge continues to build along the extending interface. From the SEM image, the active material has a very uniform structure of unblocked pores.

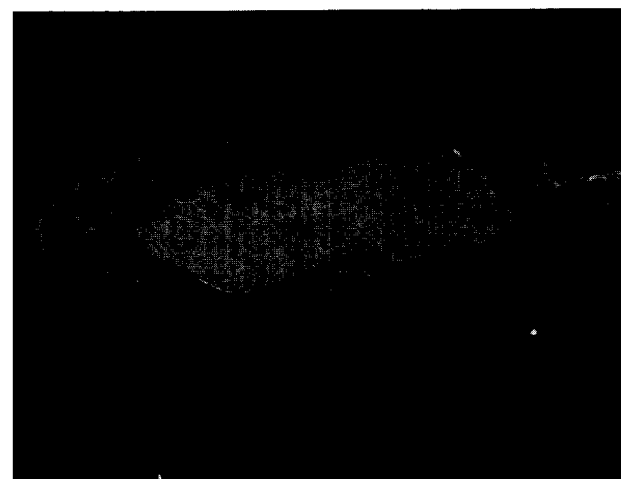Fig. 2. Chemical Ag$_2$O electrode at 10% depth of discharge. A cross section at 154 ×.

Fig. 3. Chemical Ag$_2$O electrode at 50% depth of discharge. A cross section at 154 ×.

Table 1
Utilization and average voltages of Ag$_2$O electrodes at moderate current densities

Current density (mA cm^{-2})	Temp. (°C)	Av. voltage (vs. Zn(Hg))	Utilization (% of theoretical)
40	7	1.485	96
40	40	1.559	94
80	7	1.493	92
80	40	1.551	96
120	7	1.514	93
120	40	1.517	97

Fig. 4. Chemical Ag₂O electrode at 5% depth of discharge. Planar view at 34×.
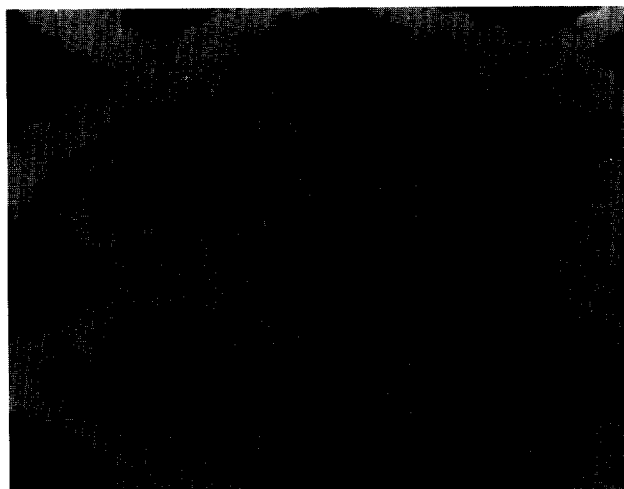
Fig. 6. Chemical Ag₂O electrode at 5% depth of discharge. A cross section SEM image at 1500×.

Fig. 5. Chemical Ag₂O electrode at 50% depth of discharge. Planar view at 34×.

Fig. 7. Chemical Ag₂O electrode at 50% depth of discharge. A cross section SEM image at 1500×.

The electroformed sintered-type electrode, however, has a reaction site at the *surface* of the electrode, rather than at the grid interface, as is the case with the chemical Ag₂O electrode. Wales [11] presented LOM section images which clearly showed the reaction at the electrode surface–electrolyte interface for 0.8 mm thick electroformed sintered plates at a 50% depth of discharge at 90 mA cm⁻² at approximately 25°C. The reduction of AgO had not taken place at the grid interface.

We believe that the excellent utilization under the test conditions is in large part due to the ready access of electrolyte through the open pore structure and to the extremely high resistivity (10⁸ ohm cm) of Ag₂O. The very low electronic conductivity forces the reaction to occur at the grid interface, and the ready access of the electrolyte provides the required water reservoir for reduction to take place at the interior of the electrode. Since the reaction zone progresses from the inside out, leaving a trail of conductive, reduced, silver behind, the electrodes discharge with very high efficiency.
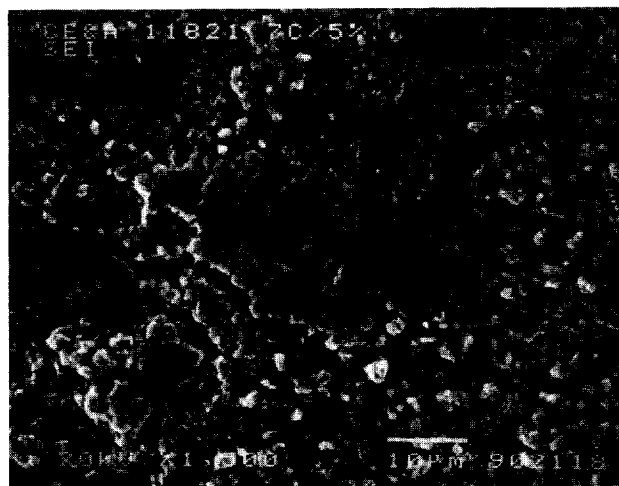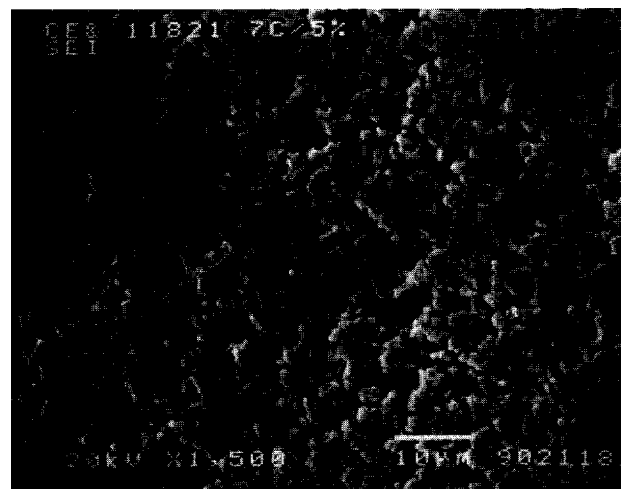
6. Vibration tests

The ability of the electrodes to withstand both handling and the battery non-operating environments was explored in a simple sine vibration test which roughly approximated to these conditions. Electrodes (23 mm×33 mm) were wrapped in a separator, then placed in a vibration test fixture. The compression of a typical cell was approximated by allowing 0.008 mm clearance for each electrode/separator assembly. Electroformed sintered electrodes were included for comparison.

The vibration fixture with electrodes was then subjected to sine vibration per MIL-STD-883, method 2007; three sweep cycles (X, Y and Z axes) from 10 to 2000 to 10 Hz at 20 g peak acceleration. Each cycle was 20 min in duration. The electrodes were subsequently removed from their separator wraps and weighed. The weight loss values are given in Table 2.

Table 2

Weight loss of chemical Ag₂O and electroformed sintered electrodes after vibration tests

Electrode type	Initial weight (g)	Final weight (g)	Wt. loss (worst case) (%)
Chemical Ag₂O	0.8503	0.8484	0.33
Chemical Ag₂O	0.7436	0.7450	0
Electroformed sintered	1.1231	1.1234	0
Electroformed sintered	1.1522	1.1525	0

Table 3

Utilization and average voltage for chemical Ag₂O electrodes discharged at high rate and at 7°C

Current density (mA cm⁻²)	Temp. (°C)	Average voltage (V)	Utilization (% of theoretical)
200	7	1.430	96
500	7	1.400	93

7. High rate discharge of Ag₂O electrodes

Silver(I) oxide electrodes are not generally regarded as being capable of high rate performance. However, as shown in Fig. 8, the electrodes perform well at very high rate. Silver(I) oxide electrodes were prepared and discharged as previously described. The test assemblies were preconditioned at 7°C prior to and during the discharge tests. The utilization and average voltage are shown in Table 3.

8. Chemically prepared AgO electrodes

Electrodes were prepared by using chemically prepared AgO (from Ames Goldsmith Company), in the identical procedures previously described for Ag₂O. Additionally, a commercial electroformed sintered electrode of similar thickness was discharged under identical conditions as a control. The galvanostatic discharges were performed at 500 mA cm⁻² and 7°C. The voltage/time data are shown in Fig. 9. The average voltages and energy densities are given in Table 4. The utilization is based upon the total weight of the electroactive mass, *exclusive* of grids. The energy density is based upon the total electrode weight and volume, *inclusive* of the grids.

As shown in the data, the chemically prepared oxide electrode discharges at near 100% utilization while the electroformed sintered electrode discharges at about half the theoretical value. It is probable that the actual electrode discharge efficiency of the electroactive material is similar for both types of electrodes, but the *charge* efficiency is limiting.
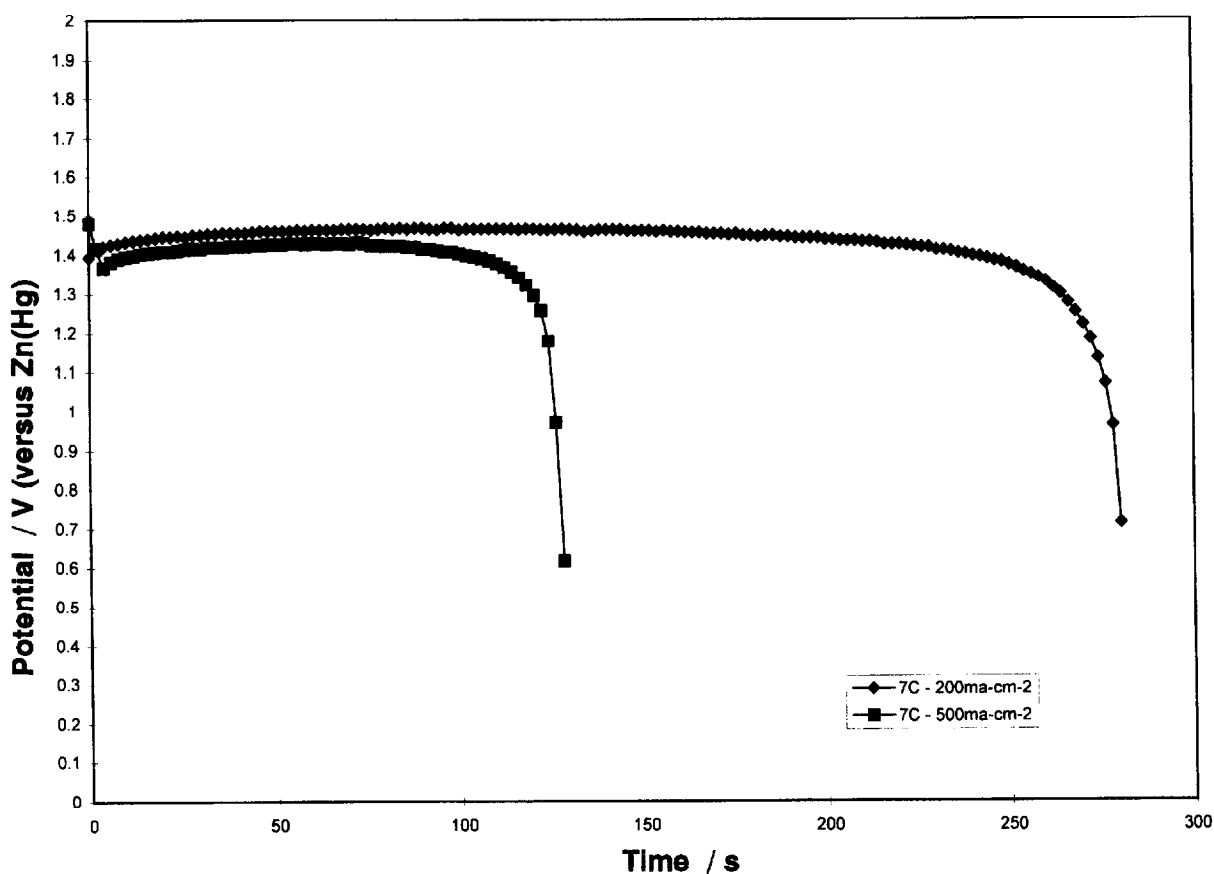

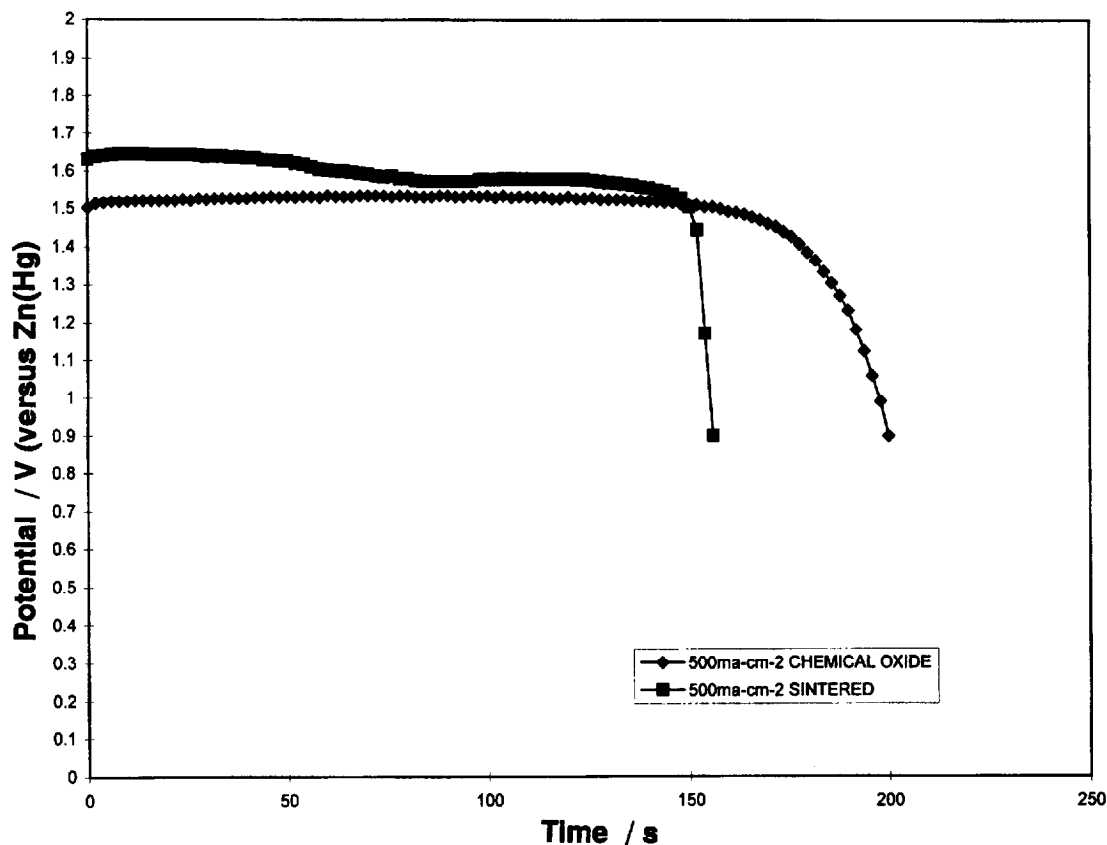Fig. 8. Ag₂O electrodes discharging at high current densities, +7°C.

Fig. 9. Chemically prepared AgO and electroformed sintered electrodes discharging at 500 mA cm^{-2}, +7°C.

Table 4
Discharge performance of chemical AgO and electroformed sintered electrodes at 500 mA cm^{-2} and 7°C

Electrode type	Average voltage (V)	Utilization (Ah g^{-1})	Energy density	
			gravimetric (mWh g^{-1})	volumetric (mWh cm^{-3})
Chemical AgO	1.526	0.4284	0.2964	2.5847
Electroformed Ag	1.594	0.2335	0.1633	1.8245

9. Summary

High rate electrodes made from chemically prepared silver oxides appear to be capable of discharging continuously with very high efficiency at rates up to 500 mA cm^{-2} at temperatures between +7 and 40°C. High efficiency beyond the reported current density and temperature envelope is now expected. Since both mono- and divalent oxide electrodes discharge well at high rate, the monovalent oxide can be used to advantage in applications where the thermal instability of AgO cannot be tolerated.

Chemically prepared silver(II) oxide electrodes discharge at slightly better utilization than the chemical silver(I) electrodes. The load voltage of the chemical divalent electrodes under discharge at rates less than 500 mA cm^{-2} is slightly lower than the electroformed sintered electrodes, but these chemical divalent oxide electrodes have been demonstrated to deliver a distinct energy density advantage (42%) over the sintered type structures.

Silver(I) oxide electrodes also operate at high efficiency and low polarization. The electrodes will be useful in applications where the battery performance after ageing is critical.

References

[1] J. Passaniti and S.A. Megahed, in D. Linden (ed.), Handbook of Batteries, McGraw-Hill, New York, 2nd edn., 1995, p. 12.2.
[2] D. Smith and G.R. Graybill, US Patent Applic. No. 60/021 384.
[3] D. Smith and G.R. Graybill, US Patent Applic. No. 60/021 552.
[4] N.T. Wilburn, in A. Fleisher and J.J. Lander (eds.), Zinc-Silver Oxide Batteries, Wiley, New York, 1971, p. 209.
[5] N.T. Wilburn and C.J. Bradley, Dry process divalent silver oxide electrodes, Tech. Rep. ECOM-2749, US Army Signal Corps., Fort Monmouth, NJ, USA, 1966.
[6] J.R. Coleman and T.E. King, in D.H. Collins (ed.), Power Sources, Vol. 1, Pergamon, 1967, p. 193.
[7] M. Lang, Proc. 23rd Power Sources Conf., Atlantic City, NJ, 1969, p. 84.
[8] A.N. Mansour and S. Dallek, J. Electrochem. Soc., 137 (1990) 1467.
[9] M. LeBlanc and H Sachse, Phys. Z., 32 (1931) 887.
[10] S. Dallek, W.G. Cox and W.P. Kilroy, Proc. 37th Power Sources Conf., Cherry Hill, NJ, The Electrochemical Society, Pennington, NJ, 1996, p. 31.
[11] C.P. Wales, J. Electrochem. Soc., 116 (1969) 729.