

Rechargeable zinc–carbon hybrid cells

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Abstract

A rechargeable zinc–carbon–bromine–complex cell with an immobilised electrolyte is described. The cell resembles a cylindrical Leclanché cell with an outside zinc can and a carbon-rod containing bobbin. A membrane-type separator prevents shorting on charge. Unlike a Leclanché cell, which has a very limited rechargeability, this zinc–carbon–bromine–complex system can deliver high currents with excellent rechargeability after many complete discharges and is insensitive to cell reversal. Organic complexing agents and additives bind or intercalate the bromine which is formed on charge and overcharge. ‘Hybrid cells’ with MnO₂ and graphite-containing cathodes have a useful initial capacity and show a better shelf-life than the simple zinc–carbon–bromine system.

Keywords: Zinc anode secondary batteries; Bromine complexes

1. Introduction

The zinc–carbon–bromine battery has a long history, dating back to the 19th century when it was used as a powerful primary battery in military applications. Many patents have been issued for later designs, most noticeable are those which describe the improvements made by Zito [1]. However it failed to satisfy safety and practical user requirements until the bromine–complex chemistry was developed by Exxon [2]. It is based on the ability of some liquid and solid organic nitrogen compounds to bind up to nine bromines per molecule, thereby lowering the bromine vapour pressure close to the level of the zinc bromide solution. The cell operates in a temperature range from –10 to 55°C.

The principle disadvantage, which up to now prevented the use of this system as a replacement of other rechargeable, small-format, batteries for general consumer use, was its high self-discharge.

In our improved version, manganese dioxide and graphite are added, creating a ‘hybrid system’ with acceptable shelf-life characteristics. This way the cell is also in a charged condition when manufactured and stored afterwards. The

graphite operates as an additional intercalation substance for bromine and, importantly, provides also more conductivity. The cell has some overcharge properties, making charge equalisation possible.

Historically, development work on carbon-based bromine electrodes with conductive plastic backing for use in fuel cells was done at the Technical University of Graz [3]. Processes for bipolar stack sealing were developed by S.E.A., Austria [4]. The development of large zinc–bromine–complex systems with circulating ZnBr₂ electrolytes made it possible to build batteries for electric vehicles which are now in the forefront of designs for future electric automobiles, outperforming the lead–acid battery in respect to capacity per weight by a factor of 2 to 3. This, at practically equal cost and having the distinct advantage that: ‘the last drop of circulating electrolyte containing the complex is as good as the first one’, meaning that the battery has about the same power performance in fully charged and nearly discharged condition. Energy density figures are between 75 and 100 Wh kg^{–1}, with power densities up to 100 W kg^{–1}. Maximum power obtained on test was 200 W kg^{–1}. Cycle life of laboratory cells have given up to 2000 cycles, while 20 kW batteries have achieved 500 cycles [5,6]. The firm which is developing such electric vehicle batteries is Powercell Corp. [7].

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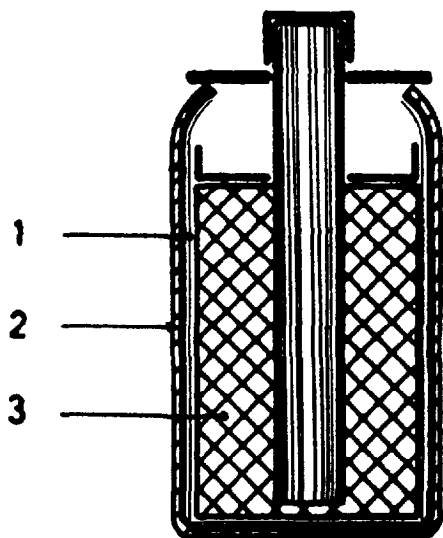


Fig. 1. The design of a cylindrical zinc-carbon-bromine-complex cell: 1, separator; 2, zinc can; 3, bobbin.

2. Comparison of small format zinc-carbon-bromine-complex cells with other rechargeable cells

Extensive work on rechargeable bipolar zinc-carbon-bromine-complex batteries was done by Manassen and Cabasso [8]. The energy and power densities achieved were excellent. Part of the success was the use of acrylic matrix substrates to bind the electrolyte. However, the high self-discharge rate persisted and up to now no new progress was reported in that respect. Manassen reported on the relation between layer thickness and self-discharge, but was still optimistic about his design [9].

We did not use thin layer structures and used the conventional central bobbin design in order to avoid the obviously existing diffusional bromine-vapour-shuttle discharges, which create losses in capacity.

The choice of the cylindrical 'D'-size (and larger ones in the future) was made on the basis of niche-consumer applications and acceptance. The capacity which can be achieved in a (limited volume) bobbin cell is low, compared to a battery using circulating zinc bromide electrolyte, where the

size of the electrolyte reservoir determines the capacity. It is also only a fraction of the capacity achieved with rechargeable alkaline manganese dioxide-zinc (RAM™) batteries, which were presented by Kordesch et al. at the 18th International Power Sources Symposium in 1993 [10]. In the meantime they captured over 50% of the rechargeable consumer cells in the USA under the trade name RENEWAL (Manufacturer: Rayovac Corp., Madison, WI). Publications about RAM cells and charging methods for consumer and OEM applications are listed in Refs. [11–13].

However, the potentially very low-cost zinc-carbon-bromine-complex system is capable of surpassing by a large margin the continuous load performance of 'D'-size Leclanché batteries. This feature of continuous current performance at very stable voltages in the range of 1.5–1.3 V is a large benefit to the user. Fig. 1 shows the design of a zinc-carbon-bromine-complex cylindrical cell and Fig. 2 shows a performance comparison with a standard zinc-carbon 'D'-size cell. The Leclanché curves are taken from Ref. [14].

3. Discussion of the principle of operation

We may distinguish between an 'external hybrid', in which two independent cells are just connected in parallel by wiring, and an 'internal hybrid' where the conductive substrate (that is, the mixture of graphite and active carbon) and the electrolyte composition are shared. A well known example for the latter is the combination of an air-carbon electrode and a manganese dioxide-graphite electrode. In this case the electrolytes can be alkaline or acidic, although KOH is better.

The zinc-bromine-carbon cell can only use an acidic electrolyte of a low pH value (3–4). The preferred electrolyte salt is zinc bromide; in practical cells we used it in 1–3 molar solutions. Mixtures are also useful; as an example: the addition of ammonium chloride improves the low temperature performance. (Such electrolytes are also very suitable for the performance of manganese dioxides, especially CMD-types.) The complex molarities may be from 0.1 to 3 molar, in various volume mixtures, mostly 1 to 1 of MEP (Br) and

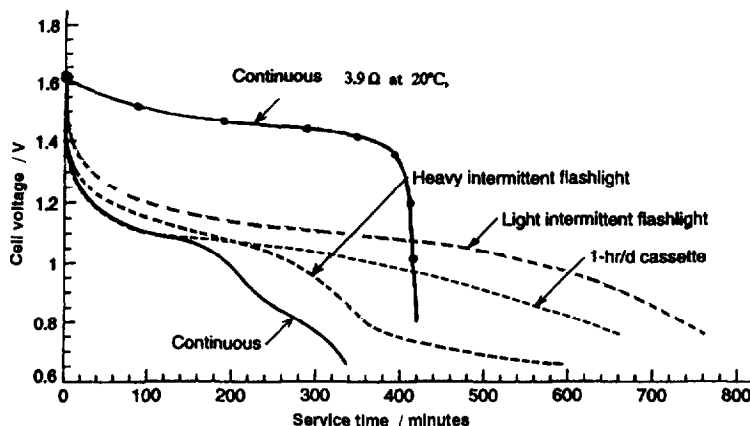


Fig. 2. Performance comparison of 'D'-size zinc-bromine-complex cells with general purpose zinc-carbon (Leclanché) cells. Specification, also continuous and intermittent discharges into 3.9 ohm.

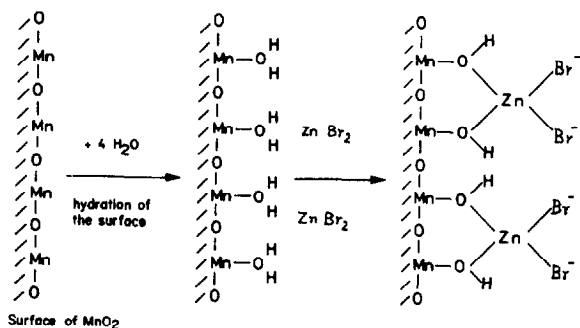


Fig. 3. Mechanism of the ion-exchange reaction on the surface of MnO₂ [14].

MEM (Br). MEP stands for methylethyl-pyrrolidinium and MEM for methylethyl-morpholinium.

Both substances have the proper temperature/vapour pressure curves and are not poisonous.

Similar bromine compounds are used in fire extinguishers. Spilled electrolytes from charged cells can be treated with bicarbonates and so made harmless for the environment with no disposal problems. The literature [1,2,5,6] lists many types of bromine complexes — only a few of them have been studied in real batteries. Solid bromine-complexing agents are also well known. The interaction of the bromine complexes with the ion transfer at the MnO₂ interface has not been reported to date, but tentatively, for comparison purposes, the model by Kozawa for ZnCl₂, and discussed in Ref. [15], is shown in Fig. 3 with ZnBr₂ as electrolyte. Also, one of us (Christoph Fabjan) has shown that bromine complexes contain zinc in various ratios, depending on the discharge state of the electrolyte.

4. Experimental data

4.1. Laboratory testing

The data in Figs. 4 and 5 were obtained from laboratory studies performed at ESTCO, Canada. Fig. 4 shows the

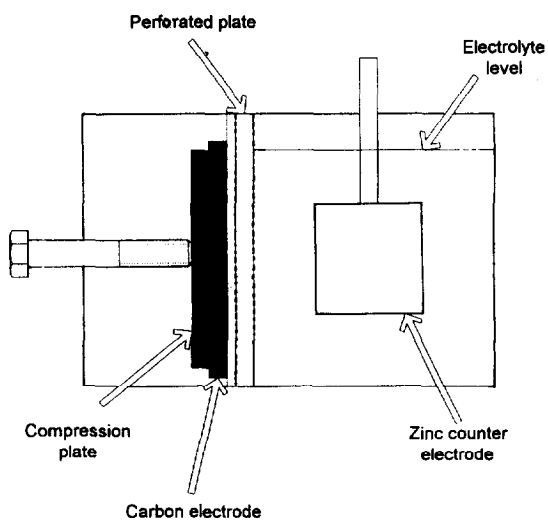


Fig. 4. ESTCO electrochemical cell for rechargeable zinc-carbon studies.

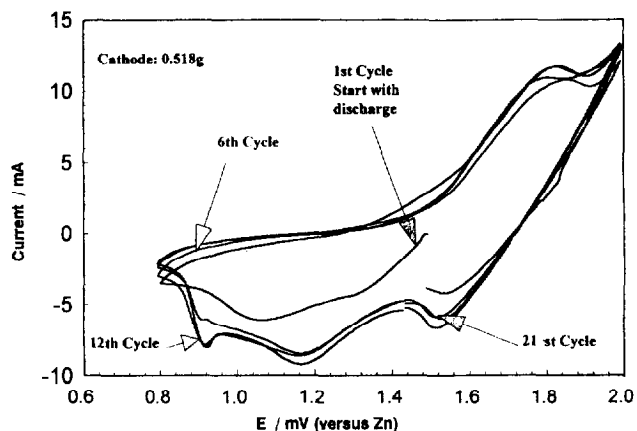


Fig. 5. Cyclic voltammety of 15% EMD + 85% acetylene black with 3 M ZnBr₂ (pH = 2.8) Scan rate = 0.1 mV s⁻¹, *T* = ambient.

ESTCO electrochemical cell for rechargeable zinc-carbon studies. Fig. 5 presents an example of cyclic voltammety curves made at ESTCO. Studies of the new complexes and experiments with intercalation materials were made in Austria at the Institute for Technical Electrochemistry, Technical University of Vienna, evaluating their uses for batteries.

4.2. Practical testing

Figs. 6, 7 and 8 show the results of testing at Battery Technologies, Inc. Fig. 6 shows cycling of a zinc-bromine-

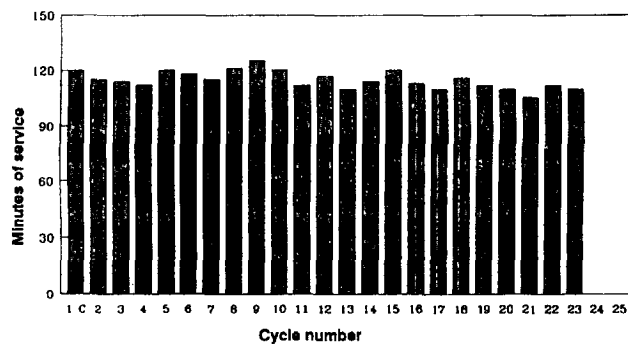


Fig. 6. Complete discharges to zero volts through 3.9 ohm of a zinc-carbon-bromine-complex 'C'-size cell containing no MnO₂. Carbon: acetylene black. Electrolyte: 3 M ZnBr₂ with 50% MEP and MEM (1:1).

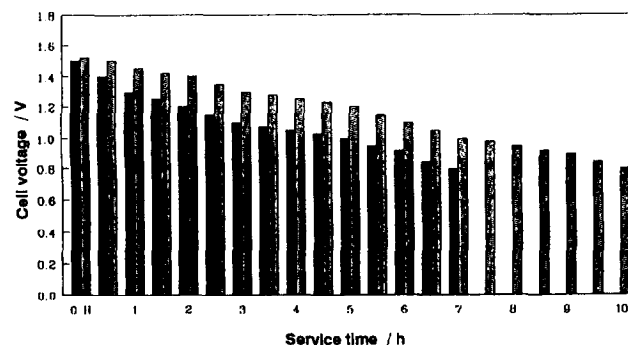


Fig. 7. First and second cycle of an immobilized zinc-bromine-complex 'D'-size cell with MnO₂. The first discharge (0.2 A, lamp) is supported by MnO₂ only (capacity ~ 1.4 Ah to a cut-off voltage of 0.8). The second cycle was obtained after charging to 1.95 V.

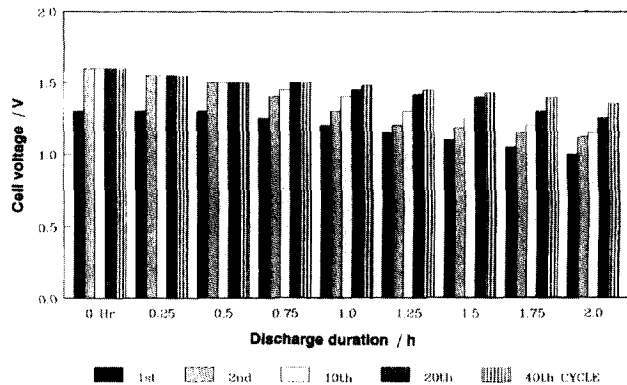


Fig. 8. Partial discharge (2 h through 3.9 ohm) and recharge to 1.9 V of a zinc-bromine-complex 'D'-size cell with MnO_2 and graphite. Note the increasing voltage of the cell with cycling.

complex 'C'-size test cell without MnO_2 addition and Fig. 7 shows the first and second cycle of a zinc-bromine-complex 'D'-size test cell with MnO_2 addition. Fig. 8 shows the effect of limited cycling of a zinc-carbon-bromine-complex cell with MnO_2 and graphite.

5. Summary

Efforts to develop rechargeable batteries are in line with the increasing trend to reduce the numbers of throw-away single-use consumer batteries, which today number over 15 billion (10^9) per year worldwide. Over half of these single-use batteries are still of the Leclanché type. Up to now, recharging Leclanché cells has not been very successful. However, recent reports from China indicate renewed, increasing, efforts with MnO_2 - ZnCl_2 - Zn batteries. There have also been attempts to use ZnSO_4 electrolytes [16] which are considered to be better than regular Leclanché electrolytes. We found a surprisingly efficient way of recharging Leclanché batteries with membrane separators.

When discharging to a depth of 30% we used intermittent charging (15 min on, 15 min off). This agrees with the known diffusion problems and recovery effects within the thick bobbin cathodes of 'D'-size cells [17]. Complete discharge destroyed the recharge capability.

The demonstrated performance of the zinc-bromine-complex cells with active carbons and graphites and the improvements obtained by adding manganese dioxide points to a chemical interaction mechanism, which will be further studied. The self-discharge has been greatly improved (probably by intercalation processes) compared to earlier cells, but there is no final judgement possible at the present time. Higher temperature tests have still to be done. We have still to find the best-suited type of separator. The cost question may be answerable after the optimal performance/concentration ratios of the complexes have been determined. The complexes are relatively expensive, however they can easily be recov-

ered by distillation of recycled scrap materials. From a production point of view, it seems possible to produce commercial zinc-carbon hybrid cells on existing manufacturing equipment for Leclanché batteries.

6. Acknowledgements

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References

- [1] R. Zito, The Zito Co., *US Patent Nos. 3 285 781; 3 382 102; 3 640 770; 3 719 526* (1966–1973).
- [2] D.J. Eustache and P.A. Malachuk (Exxon), *US Patent Nos. 4 064 324* (1977); *4 068 046* (1977).
- [3] K.V. Kordesch, A. Wertgarner, Ch. Fabjan and G. Tomazic, in *Conf. Proc. 88-11*, The Electrochemical Society, Pennington, NJ, 1988, pp. 293–304; A. Wertgarner, *Zinc-Bromine, Dissertation*, TU-Graz, 1987.
- [4] G. Tomazic, *Oesterr. Chem.-Z.*, 87 (4) (1966) 104.
- [5] Ch. Fabjan, The zinc-bromine energy storage system: state of the art, safety, recycling and future, *Proc. 13th Int. Seminar Primary and Secondary Battery Technology and Applications*, Boca Raton, FL, Mar. 1996.
- [6] G. Tomazic, Zinc-bromine systems for EV-batteries, *Electrochem. Soc. Meeting, San Antonio, TX, 6–11 Oct. 1996*, Abstr. No. 602 (extended paper in ECS book format (1996)).
- [7] Brochures *The Zinc-Flow Battery and Wave Power Station*, Powercell GmbH, Cambridge, MA, USA.
- [8] J. Manassen and I. Cabasso, Thin, ribbonlike flexible rechargeable zinc/halide cell, *US Patent No. 5 011 749* (30 Apr. 1991).
- [9] J. Manassen, *Prototypes of a Rechargeable Circulation-free Zinc Bromine Cell*, Department of Materials and Interfaces, The Weizmann Institute of Science, Rehovot, Israel; New aqueous high energy and power density batteries, *Project Rep.*, 1991.
- [10] K.V. Kordesch, L. Binder, W. Taucher, C. Faistauer and J. Daniel-Ivad, in A. Attewell and T. Keily (eds.), *Power Sources 14*, International Power Sources Committee, Crowborough, UK, 1993, p. 193.
- [11] K. Kordesch and M. Weissenbacher, *J. Power Sources*, 51 (1994) 61–78.
- [12] K. Kordesch and J. Daniel-Ivad, Rechargeable manganese dioxide batteries, *Proc. 37th Power Sources Conf., Cherry Hill, NJ*, The Electrochemical Society, Pennington, NJ, 1996.
- [13] J. Daniel-Ivad and K. Kordesch, The status of the rechargeable alkaline manganese dioxide/zinc battery, *190th Electrochem. Soc. Meet., San Antonio, TX, 6–11 Oct. 1996*.
- [14] D. Linden (ed.), *Handbook of Batteries*, McGraw Hill, New York, 2nd edn., 1995, Chs. 8 and 37.
- [15] R. Huber, in K. Kordesch (ed.), *Batteries, 1: Manganese Dioxide*, Marcel Dekker, New York, 1974, Ch. 1, Fig. 11, p. 34.
- [16] M.H. Askar, H. Abbas and S.E. Afifi, *J. Power Sources*, 48 (1994) 303–309.
- [17] H. Neuhertz, Leclanché battery charging, *Internal Rep.*, Battery Technologies, Inc., 1995.