

Magnesium-lead chloride batteries

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The preparation of lead chloride cathodes, and their discharge in magnesium-lead chloride batteries, is described. The lead chloride blended with graphite is pasted on grids of expanded copper, using urea formaldehyde solutions as the binder. One-, five-, and fifteen-cell batteries were discharged at temperatures between -40°C and $+45^{\circ}\text{C}$, at low current drains. For five-cell batteries energy densities in the range 10-30 Wh/lb were obtained. Mechanical properties of the cathode, so far as investigated, were excellent. The main difficulty was cathode softening during prolonged runs at high temperatures. At -40°C the battery attained working voltage in about 5 minutes; although slower than the Mg-AgCl system, the Mg-PbCl₂ system should meet many applications at this temperature.

Introduction

Lead chloride was first mentioned as a cathodic material in a Russian patent describing magnesium-lead chloride batteries [1]. Performance characteristics were subsequently published for several sea-water activated batteries intended for radiosonde and emergency (lighting and signalling) applications and employing silver, lead and cuprous chlorides as the cathode [2]. Nomura *et al* [3] had meanwhile published details on the construction of multi-cell batteries employing lead chloride cathodes. They reported excellent cathode utilization in accordance with the reaction: $\text{PbCl}_2 + 2e \rightarrow \text{Pb} + 2\text{Cl}^-$.

In agreement with the standard potentials of the Pb/PbCl₂ and Ag/AgCl couples, -0.268 V and $+0.222$ V respectively [4], the Mg-PbCl₂ system in aqueous chloride electrolyte has a potential about 0.5 V lower than the Mg-AgCl system under the same conditions, this being 1.05 V [3] as compared to about 1.54 V at room temperature and for moderate current drains.

This paper presents experimental details on the development of lead chloride cathodes for the magnesium-lead chloride system, its incorporation in several multi-cell series-connected batteries, and their performance.

Experimental methods and results

General

It has been common practice to prepare AgCl cathodes for low to moderate drain applications by rolling out the fused material into sheets [5]. Silver tabs are attached and initial conductivity is imparted by reduction of a thin surface film of AgCl. One such cathode is inserted between two Mg or Mg-alloy anodes, alloys of the AZ31 and AZ61 series being commonly used, with physical separation being maintained by spacers. The cell is then wrapped or encased, provision being made for the entry of electrolyte and the removal of hydrogen and sludge resulting from magnesium corrosion. This is accomplished by inserting ports in the top and bottom of the cell. These general procedures are followed here with the difference that, as in previous work [3], the lead chloride cathode was prepared by blending the material with conductive carbon and a binder, and spreading the mixture on a metallic current collector.

Cathode preparation

Lead chloride, ground and screened to pass 100

mesh, was dry blended with a variety of conductive carbons, the PbCl_2 comprising 80% or more of the total. Powdered graphite was found most suitable, and all the work reported here was done using one commercial graphite.* Of a number of organic binders examined, an aqueous solution of urea and formaldehyde was most satisfactory. Four volumes of aqueous urea solution (usually 5%, 10% or 20% w/v) were mixed with three volumes of aqueous formaldehyde of the same concentration, and a sufficient amount of this solution added to the dry mix to form a viscous, non-settling paste. (For 10 g of dry mix containing PbCl_2 and C in the ratios 80–20, 85–15, 90–10 and 95–5, this was approximately 3.8, 3.5, 2.8 and 2.0 ml respectively, these volumes depending on the PbCl_2 –C ratio and only slightly, if at all, on binder concentration.) Plates were pasted up on both sides of an expanded copper grid† held in a lucite ‘window-frame’ mould which rested on a flat base. After drying to a weight loss corresponding to approximately $\frac{2}{3}$ to $\frac{3}{4}$ of the water originally present in the binder, the plate was pressed at 1000 to 3500 psi with a lucite block cut to fit the mould. No advantage was found in employing greater pressures. A tab for electrical connection was left on an upper corner of the copper grid, and a slight recess to accommodate it cut in the corresponding corner of the lucite block. The plate was then expelled from the mould, air-dried 24 h or longer, and cured at 110°C for 48 h, under slight pressure to prevent warping.

Considering the molecular weights of urea and formaldehyde (60 and 30), a 4/3 volume ratio of, for example, 20% urea and 20% formaldehyde represents a mole ratio of 2/3, close to that reported in actual resins [6]. Deviation from this ratio, especially in the direction of excess formaldehyde, results in poorer mechanical properties and shorter run times for the cathodes.

These cathodes and the cells made from them have not yet been subjected to environmental testing. They are, however, sufficiently hard to be drilled and sawn without splintering; plates

* 6353 (Micro 850), a product of Asbury Graphite Mills, Asbury, N.J.

† 5 Cu 7–4/0, or 3 Cu 7–4/0, a product of the Exmet Corp.

similar to those of run 23, Table 3 (of which a considerable number have been tested), have been dropped from a height of about four feet with only minor damage at the point of impact. They have been discharged without deterioration in performance after 10 weeks summer storage, and 10 months storage over desiccant.

Single-cell discharges

A number of single cathodes were discharged against two magnesium-alloy anodes, in excess electrolyte, at an anode–cathode separation of 0.060 in. Two sizes of cathode were employed, 1.5 in \times 2.0 in, and 2.50 in \times 2.75 in. Variables were temperature, PbCl_2 –C ratio, plate loading, urea-formaldehyde concentration, current density, Mg alloy, and electrolyte. The electrolyte was usually synthetic sea-water; below 0°C a LiCl electrolyte was used. At our rather low current densities, cell voltages were of the order of 1.05 V at room temperature and above, 1.0 to 0.9 V at 0°C and 0.9 to 0.7 V at –40°C. The percentage utilization to the various end-voltages (1.0, 0.9, 0.8, 0.7 V) was calculated from the dry mix composition and the known weights of cathode, grid and binder. The weight of binder in the cathode was obtained with sufficient accuracy by evaporating known volumes of urea-formaldehyde solution to dryness, curing, and weighing the residue. In all runs in this work except run 39, to be described below, the electrolyte and the cell or multi-cell battery were separately equilibrated at the run temperature, the cell activated on open circuit and after 1 to 2 min discharged at constant impressed current, the voltage being recorded with conventional equipment.

A few of the results with single cells are listed in Tables 1 to 3, grouped according to discharge temperature. In column 3, plate loading is expressed as grams of dry mix per in² of mould cavity (thus, for the commonest case, 10.0 g mix on a 1.5 in \times 2.0 in plate, the loading is 3.33 g/in²). Column 6 records the time required for recovery to 95% of the peak run voltage (Tables 1 and 2 only; at low temperatures a voltage drop occurs when the cell is put on load.)

With the hand-pasting method used, plates are inevitably not of uniform thickness. Vari-

Table 1. Single-cell discharges at -40°C . Electrolyte, 21% W/W LiCl in $\text{H}_2\text{O} + 0.5\%$ $\text{K}_2\text{Cr}_2\text{O}_7$; cathode, 1.5 in \times 2.0 in; anode, Mg AZ31.

Run No.	Ratio PbCl ₂ -C	Loading g/in ²	Binder conc. %	C.D., mA/in ²	Come-up time, min	Theoret. run, h	% utilization to		
							0.9 V	0.8 V	0.7 V
1	80-20	2.00	20	12.5	6	11.9	0	15	50
2	80-20	3.33	20	12.5	*	19.7	0	11	41
3	85-15	1.77	20	12.5	4	11.1	5	54	78
4	85-15	2.33	20	12.5	*	14.9	0	13	30
5	85-15	3.33	10	12.5	<1	20.1	5	65	82
6	85-15	3.33	10	24.0	9	10.3	5	8	30
7	85-15	6.67	10	12.5	4	42.6	0	14	35
8	85-15	3.33	5	12.5	11	21.3	10	61	86

* Not available.

Table 2. Single-cell discharges at 0°C . Electrolyte, 2.4% NaCl + 0.48% MgSO₄, W/V; cathode, 1.5 in \times 2.0 in; anode, Mg AZ31, unless otherwise stated.

Run no.	Ratio PbCl ₂ -C	Loading g/in ²	Binder conc., %	C.D. mA/in ²	Come-up time, sec	Theoret. run, h	% utilization to		
							1.0 V	0.9 V	0.8 V
9	85-15	1.77	20	24.0	60	5.7	44	75	88
10	85-15	3.33	20	12.5	35	21.1	0	35	83
11	85-15	3.33	10	12.5	10	21.2	5	53	98
12	85-15	6.67	10	12.5	70	41.8	0	13	83
13	85-15	6.67	10	24.9	80	20.9	0	10	74
14	90-10	2.04	20	24.0	18	7.2	0	84	92
15	90-10	3.33	20	12.5	24	22.1	0	37	94
16	90-10	3.33	10	24.9	<5	22.2	25	90	99
17*	95-5	2.18	20	24.0	75	8.08	0	90	93
18*	95-5	2.18	37	24.0	100	8.15	0	69	93
19	95-5	3.33	10	12.5	18	23.7	59	90	96
20	95-5	3.33	37	12.5	75	22.7	0	95	100
21	95-5	3.33	20	24.9	18	11.9	0	59	93

* Cathode: 2.5 in \times 2.75 in; anode: Mg AZ61.

Table 3. Single-cell discharges at room temperature. Other conditions as in Table 2, unless otherwise stated.

Run no.	Ratio PbCl ₂ -C	Loading g/in ²	Binder conc. %	C.D., mA/in ²	Theoret. run, h	% utilization to		
						1.0 V	0.9 V	0.8 V
22	85-15	1.77	20	24.0	5.6	80	94	96
23*	85-15	1.77	20	24.0	5.7	43	88	90
24	85-15	5.31	20	24.0	11.0	30	79	89
25	85-15	1.77	20	48.5	2.85	1	88	95
26	95-5	3.33	20	24.9	23.0	79	90	90
27	95-5	3.33	37	24.9	11.2	35	77	87
28†	100-0	5.00	20	12.3	37.6	61	68	70

* Cathode: 2.5 in \times 2.75 in; anode: Mg AZ61.

† Come-up time to 0.8 V: 10 sec; to 0.9 V: 2 min; to 1.0 V: 40 min.

ations over a single plate could, with practice, be reduced to $\pm 5\%$. By averaging numerous measurements on individual plates, the actual thickness, in thousandths of an inch, was found to be approximately 18, 17 and 16 times the plate loading as defined in (3) above, for 85-15, 90-10 and 95-5 mixes respectively.

The effect of increased binder concentration in lowering utilization is apparent, most notably at -40°C (*cf.* runs 5 and 8, 10 and 11, 19 and 20, of Tables 1, 2 and 3). The same effect results on increasing plate loading (*cf.* runs 1 and 2, 11 and 12, 22 and 24). Apparently only light current drains are possible at -40°C .

The effect of varying PbCl_2 -C ratio on performance is obscured by the simultaneous change in volume of binder solution necessary to make a suitable paste, as described under *Cathode preparation*; variation in amount of binder itself influences behaviour, as seen above. That some graphite is necessary for conductivity is evident from the slow come-up and poor utilization of run 28, containing 100% PbCl_2 .

In the original work at room temperature, 20% binder solutions were employed. Poor performance at -40°C led to work with lower concentrations. In later work, summarized in Tables 2 and 3, concentrations were varied from 10 to 37%, and loading, mix ratio, and current drain were also varied to determine the range of conditions in which satisfactory discharge was possible. Cathodes (not described here) made with 5% binder and 95-5 dry mix requiring therefore only a small volume of binder, were dusty to the touch; otherwise all cathodes were equally strong and coherent.

Cathodes made and discharged under the conditions described above are firm, unswollen and coherent at the end of discharge. At higher temperatures (30 – 45°C) some softening is noted, presumably due to increased PbCl_2 solubility. The extent of this depends on the length of discharge; cathodes such as 22 and 23, whose run time is about 6 h, show no shape change or loss of material after discharge at 45°C , and are rigid enough in some cases to crack on bending. However, longer exposure to electrolyte at 45°C (24 to 48 h) results in considerable swelling and detachment from the grid. This can to a certain extent be overcome by applying filter

paper to the wet surface of the cathode during manufacture, and pressing it in. The discharges, at -40°C and $+45^\circ\text{C}$ of two multi-cell batteries so made (runs 29 and 32), are described in Table 4 (A) of the next section.

Five-cell batteries

In all the batteries to be described, cathodes and anodes were 2.5 in wide and 2.75 in high. With two exceptions (runs 35 and 36) an 85 PbCl_2 -15C mix was used. Electrical leads, spot-welded to the anodes and soft-soldered to the cathode tabs, were protected with 731 RTV silastic* or pliobond cement† As before, cells consisted of one cathode and two anodes with a separation of 0.050 in or 0.040 in, and the assembly was taped together with mylar. Ports, 1 in long \times 0.063 in i.d., were inserted in two diagonally opposite corners of each cell to reduce intercell short-circuiting; this necessitated removal of a rectangular piece 0.5 in \times 0.25 in from the corresponding corners of the cathode.

Characteristics of a few of the batteries are listed in Table 4. Cathodes were prepared with two different weights of dry mix, 25.0 g and 12.2 g, for a relatively long and relatively short run time respectively (nominally 24 and 6 h). Column 7 of Table 4 lists the run time calculated from final cathode weight as described in the previous section. The figure for Wh/lb in column 11 is based on dry battery weight, and is calculated for the average battery voltage to an end voltage of 0.8 V per cell (4.0 V for the 5-cell stack). Dimensions of all the five-cell batteries used were, width 2.56 to 2.62 in, height (exclusive of leads) 3.06 to 3.12 in, and thickness varying from 0.85 in (runs 37, 38) to 1.56 in (runs 29 to 32). This last dimension varied most because of variations in anode, cathode and spacer thickness.

In two runs (29, 32) the batteries were subjected to intermittent discharge (4 h at 171 mA, 20 h on open circuit). In preparing the cathodes for these batteries, pieces of No. 1 Whatman filter paper, cut to fit the moulds, were placed on both sides of the wet cathode after pasting up.

* Dow Corning Corporation.

† GC Electronics, Rockford, Ill.

After compression, drying and curing, the edges of the plate were sealed by painting with polystyrene Q-dope*. The effectiveness of this in delaying cathode disintegration at 45°C is seen on comparing runs 32 and 33. The 8 h of run 32, moreover, is broken by 20 idle stand at 45°C.

The discharge curves for runs 29, 37 and 38 are shown in Figs. 1 and 2. The time-scale is split in Fig. 1 to bring out the details of initial voltage rise at -40°C.

Fifteen-cell battery

Characteristics of this battery are listed in Table 4 (D) (run 39), and the discharge curve is depicted in Fig. 3. In accordance with the requirements laid down for an intended application (rapid come-up at 0°C after prolonged refrigeration) the battery in this run was cold-soaked overnight at -40°C, plunged into 3% NaCl solution at 0°C, and discharged immediately, reaching 15.0 V within 10 to 15 sec. Comparison with run 37, a five-cell battery in which intercell shorting should be less, reinforces the conclusion drawn from single-cell work that improvement results on using PbCl-C ratios higher than 85-15.

The energy densities reported here compare favourably with Vyselkov's figures (10 to 11 Wh/lb); in his work current densities and

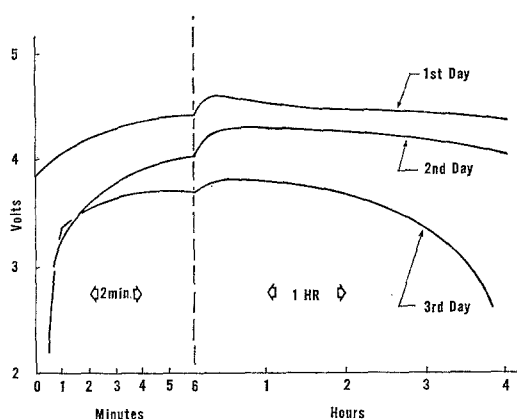


Fig. 1. Run 29. Discharge of 5-cell battery at -40°C, on intermittent drain, 171 mA for 4 h, open circuit for 20 h. Battery went into reversal for about 20 sec at start of 2nd and 3rd day's run, and failed to reach 0.8 V/cell on third day. Note time scale split at 6 mins.

* GC Electronics, Rockford, Ill.

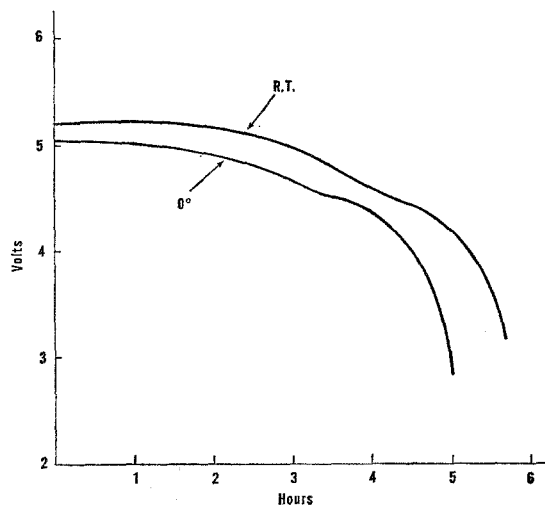


Fig. 2. Discharge of 5-cell batteries at 0°C (lower curve, run 37) and room temperature (upper curve, run 38) at 330 mA, 3% NaCl electrolyte. Batteries reached 4.5V in 3 sec (run 37) and <1 sec (run 38). 8515 PbCl₂-C mix employed.

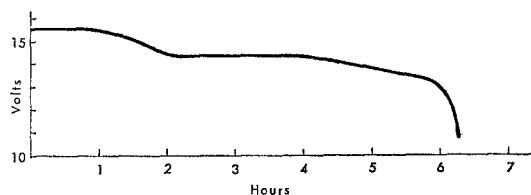


Fig. 3. Run 39. Discharge of 15-cell battery at 0°, 330mA, 3% NaCl electrolyte. Battery, cold-soaked overnight at -40°C, reached 15 V in 10 to 15 sec. 90-10 PbCl₂-C mix employed.

battery voltages are considerably higher, so that losses due to polarization and intercell shorting are more severe. With attention to design, the system is evidently capable of satisfactory energy densities even at -40°C.

Discussion

In comparing the Mg-AgCl and Mg-PbCl₂ systems, the lower voltage of the latter, necessitating half as many cells again for the same battery voltage, is the main drawback and tends to offset the relative cheapness (c. \$0.20/lb) and availability of PbCl₂. PbCl₂ and AgCl have nearly the same density (5.85, 5.56 g/ml) and equivalent weight (139, 143). However, while

Table 4. Multi-cell battery discharges.

(A) 5 cells; electrolyte $\text{LiCl-K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{O}$; 25.0 g 85-15 dry mix/plate; separation 0.050 in.(B) 5 cells; electrolyte $\text{LiCl-K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{O}$; 25.0 g 95-5 dry mix/plate; separation 0.050 in.

(C) 5 cells; electrolyte 3% NaCl; 12.2 g 85-15 dry mix/plate; separation 0.040 in.

(D) 15 cells; electrolyte 3% NaCl; 14.0 g 90-10 dry mix/plate; separation 0.040 in.

Run no.	°C	Binder conc., %	Current mA	Mg Alloy	Mg Thickness, in	Theoret. run, h	h Actual to 0.8 V/cell	Coulombic eff. to 0.8 V/cell	Dry Wt, lb	Wh/lb
(A)										
29*	-40	5	171	AZ31	0.0425	22.9	8.0	35	0.58	10
30	-40	5	200			19.05	9.2	48	0.58	14
31	-40	10	200			19.0	8.1	43	0.58	12
32*	45	5	171			22.2	8.0	36	0.58	12
33†	45	10	200	AZ61	0.020	18.9	3	16	0.48	5.5
34	0	10	200			19.2	12.8	67	0.46	26
(B)										
35	-40	20	200	AZ61	0.011	22.4	6.7	30	0.42	13.5
36	-40	10	200			22.4	8.9	40	0.42	18
(C)										
37	0	20	330	AZ61	0.011	5.7	4.5	79	0.29	24
38‡	23	20	330			5.7	5.3	93	0.29	28
(D)										
39	0	20	330	AZ61	0.011	7.25	6.25	86	0.93	32

* Intermittent discharge, 4 h at 171 mA/20 h off; cathode encased in filter paper failed to reach 0.8V/cell at start of third day's discharge.

† Cathode disintegrated after several hours run at 45°C.

‡ Temperature quoted is ambient; battery temperature is undoubtedly higher.

the density of rolled AgCl sheets is virtually the theoretical value, and in principle all the material is available for discharge, there is considerable pore volume in the PbCl_2 cathode. A series of thickness and weight measurements were carried out on PbCl_2 cathodes made with a loading of 3.33 g/in² using 10% urea-formaldehyde. These, when combined with known or reasonable densities for the components of the cathode (PbCl_2 , 5.85 g/ml; Cu, 8.92; carbon, *c.* 2.2; binder, *c.* 1.5) lead to the approximate volume percentages of components shown in Table 5. These figures are little affected by varying pressure in the range 1400 to 3500 psi. Thus it is seen that lead chloride plates must be appreciably thicker than AgCl plates of the same coulombic capacity.

Two other disadvantages must be mentioned,

the first being the relatively slow come-up time at -40°C (see Fig. 1). This has been obviated in single-cell work by incorporating a few per cent of Ag_2O in the mix; however, binders other than urea formaldehyde, e.g. carboxymethyl cellulose, must be used, as Ag_2O is reduced by formaldehyde. The second disadvantage is the disintegration during prolonged runs at high temperatures. The expedient of sealing the

Table 5. Volume percentage of components in pasted $\text{PbCl}_2\text{-C}$ cathodes.

Mix ratio	PbCl_2	C	Cu	Binder	Void (by difference)
85-15	47-49	23	3	7	18-20
90-10	50-53	15	3	5	24-7
95-5	60-61	8	3	4	24-5

cathode in filter paper (run 32) is of doubtful practicality, and in cases where dimensional restrictions are important the increased cathode thickness (c. 0.010 in) may not be negligible. Thinner (tea bag) papers have been used, but tend to pull off while the plate is curing. Subsequent sealing of the edges as described above leaves an air-gap between cathode and paper which prevents rapid wetting and in consequence ruins performance.

In conclusion, we believe that in selected applications the Mg-PbCl₂ battery can be developed as an alternative to the Mg-AgCl. The batteries described in Table 4, hand-built and unoptimized, give an indication of the capabilities of the system. A contract is under negotiation for the development of a multi-cell battery similar to that of run 39 and the production of prototypes for a sonobuoy application. From the results of this work we hope to establish methods of manufacture.

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References

- [1] A. A. Vyselkov and G. I. Rogova, *Chem. Abstracts*, **52**, 10770 (1958).
- [2] A. A. Vyselkov, I. T. Kop'yev and V. A. Naumenko, *Elektrotehnika*, **12**, 50 (1969).
- [3] H. Nomura, M. Takeuchi and H. Abe, *G. S. News*, **26**, 47 (1967). An abstract appears in *Denki Kagaku News Letter*, April, 1968.
- [4] W. M. Latimer, 'The oxidation states of the elements and their potentials in aqueous solutions', Prentice-Hall Inc., New York (1938).
- [5] I. C. Blake, *J. Electrochem. Soc.*, **99** 202C (1952).
- [6] J. F. Walker, 'Formaldehyde', 2nd ed., p. 297, Reinhold, New York (1953).