Journal of Power Sources, 1 (1976/77) 371 - 375

Preliminary Note

Preliminary report on the performance characteristics of the magnesium–mercurous chloride battery system

K. V. PRASAD, N. VENKATAKRISHNAN and P. B. MATHUR
Central Electrochemical Research Institute, Karaikudi (India)
(Received November 1976; in revised form February 19, 1977)

In the past 30 years a number of papers have been published on water activated cells with magnesium alloy anodes and insoluble metal chloride cathodes. Of the four favoured cathode materials, silver chloride [1, 2] cuprous chloride [3], lead chloride [4 - 6] and mercurous chloride [7 - 10], the last named material has received the least attention despite the fact that its electrochemical characteristics appear to be quite favourable (Table 1). Work has, therefore, been undertaken to investigate further the characteristics of this system and preliminary results of this work are now described.

TABLE 1
Comparative data on chloride batteries

System	Open circuit voltage (volts)	Working voltage (volts)	Ampere hour capacity/g	Solubility of cathodic material (g/100 ml)	Potentials of cathodes against S.H.E.
Mg–AgCl	1.6	1.55–1.3	0.183	8.9×10^{-5}	+ 0.222
Mg–CuCl	1.4	1.3 –1.1	0.270	6.2×10^{-3}	+ 0.137
Mg–$PbCl_2$	1.1	0.95–0.85	0.192	6.73×10^{-4}	− 0.268
Mg–Hg_2Cl_2	1.65	1.55–1.2	0.113	1.4×10^{-4}	+ 0.268

Experimental

Magnesium anodes, 4 cm × 2.5 cm, were made from AZ 31 magnesium alloy. A lead wire was soldered to these electrodes by a process patented earlier [11]. Unless otherwise specified, in all experiments mercurous chloride cathodes were made by pasting or pressing a cathodic mix containing

5.4 g of mercurous chloride and 0.6 g of acetylene black and a binder on a metallic grid. The size of the cathode was the same as that of the magnesium electrode. The electrodes were wrapped in paper separators as the mercurous chloride electrode is mechanically weak. Cells containing two anodes and one cathode were assembled in plastic containers. The tops of the containers had two terminals and a central hole. The cells were activated with 3% sodium chloride or 20% magnesium perchlorate solution. These cells were discharged at room temperature (29 °C + 2 °C) at different current drains. The effect of variations in the percentage of the acetylene black in the cathode mix on the discharge characteristics has also been studied. The results of these studies are presented and discussed here.

Results and Discussion

Voltage vs. *current curves*

Cells with effective electrode areas of 20 cm^2 were used for current *vs.* voltage and other discharge studies. Currents in multiples of 100 mA were drawn from the cells for a period of 30 seconds before the voltage was noted. Values of current density, instead of current, are plotted against the observed voltages in Fig. 1. Curve 1 represents the cell activated with 3% sodium chloride solution and curve 2 a cell activated with 20% magnesium perchlorate solution. It may be noted from the Figure that the slope of the curves is not steep. The two curves are extremely smooth straight lines indicating that the polarization of the cell is mainly of ohmic character. The low value of the slopes of the voltage–current curves enables the cell to discharge at high rates.

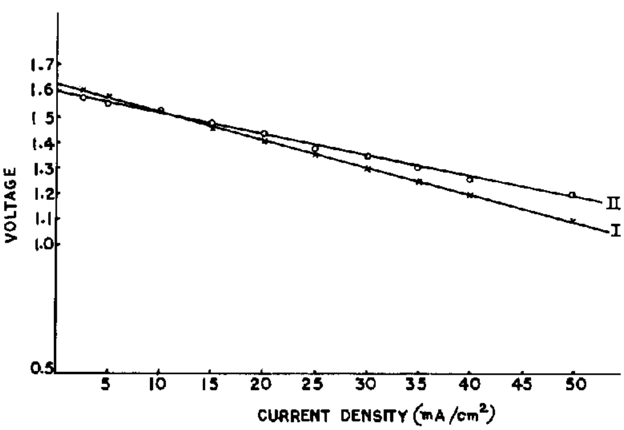

Fig. 1. Voltage–current density relationship. I, cells with 3% NaCl electrolyte (×); II, cells with 20% $Mg(ClO_4)_2$ electrolyte (○).

On short circuit the cell activated with sodium chloride electrolyte showed a voltage of 0.8 V at a current of 1.5 A, that is a current density of 75 mA/cm^2 and 60 mW/cm^2. The cell activated with magnesium perchlorate electrolyte showed a voltage of 0.875 V and a current of 1.8 A; 90 mA//cm^2 and 78.8 mW/cm^2. These characteristics indicate that the magnesium–mercurous chloride cell is a high power system useful for heavy drain applications.

Voltage vs. *time*

Three cells of identical nature were activated with a 3% solution of LR grade sodium chloride, and another three with 20% magnesium perchlorate solution. The cells were discharged at 100 mA, 200 mA and 300 mA. Voltage *versus* time curves for the cells activated with 3% sodium chloride are plotted in Fig. 2 and those with magnesium perchlorate solution in Fig. 3.

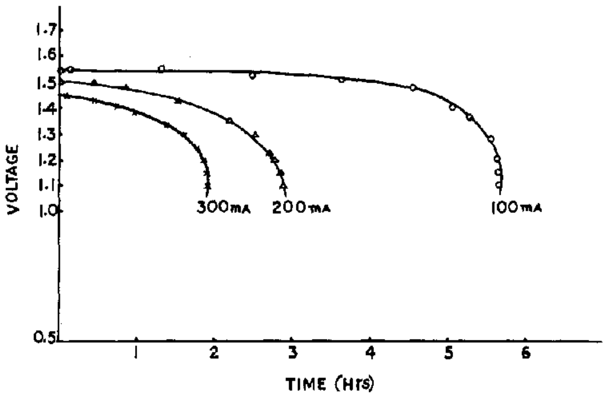

Fig. 2. Discharge of cells with 3% NaCl electrolyte. ○, at 100 mA; △, at 200 mA; ×, at 300 mA.

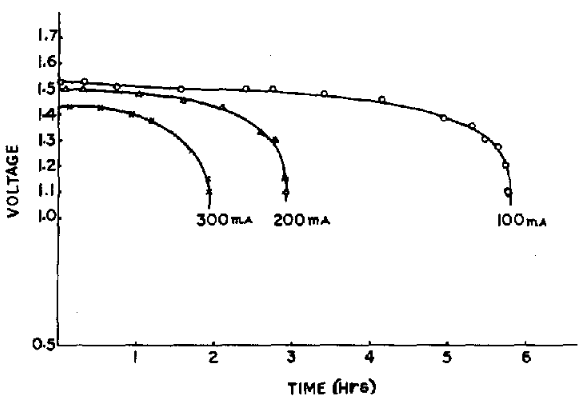

Fig. 3. Discharge of cells with 20% $Mg(ClO_4)_2$ electrolyte. ○, at 100 mA; △, at 200 mA; ×, at 300 mA.

As may be seen from these Figures, the curves are very smooth and flat at low current drains, with the slope increasing gradually with increase in current drain. It will be noted from the curves that over 90% of the cell capacity is obtained within a narrow voltage range of 1.55 to 1.2 V.

A comparison of the curves for sodium chloride and magnesium perchlorate electrolytes indicates that the cells activated with two different electrolytes possess almost the same discharge characteristics with the exception of a slight difference in the slopes of the curves at high current drains, *viz.* 200 mA and 300 mA. The cell with sodium chloride shows a somewhat steeper fall in voltage than the cell with magnesium perchlorate, although the overall capacities obtained at the different current densities are identical in the two cases. The major difference between the two cell systems, however, lies in the rates of chemical corrosion of the magnesium electrode during the operation of the two cells. A magnesium anode corrodes faster and generates larger volume of gas in sodium chloride electrolytes than in magnesium perchlorate electrolytes. But the cost of sodium chloride is very much less than that of magnesium perchlorate. Depending upon the end use, the electrolytes can be selected suitably without significantly affecting the electrical performance of the cell. For short period use and for consumer applications, sodium chloride may be preferred. But for specific long period applications, magnesium perchlorate can be a good choice.

Material utilization vs. *percentage of acetylene black in cathode mix*

The data plotted in Figs. 1, 2 and 3 were obtained with a cathode mix containing a fixed ratio of mercurous chloride and acetylene black, *viz.* 90:10. This ratio was arrived at from studies carried out on the coefficient of utilization of mercurous chloride with different percentages of acetylene black. The data obtained for the variation of the utilization with the percentage of acetylene black (ranging from 5% to 20%) in the mix are given in Table 2. The data indicate that: (a) the utilization remains as high as 86% even with as low a percentage as 5% acetylene black; (b) the utilization increases from 86% to 94% with increase in acelytene black content from 5% to 10%. Further increase in the content of acetylene black upto 15% maintains the utilization around 94% but beyond 15% it falls.

TABLE 2

Effect of acetylene black content on the material utilization of mercurous chloride

Percentage of acetylene black	Material utilization (%)
5.0	86.6
7.5	90.4
10.0	94.0
12.5	93.8
15.0	93.6
20.0	86.0

From the view point of high utilization, a 10% to 15% acetylene black is therefore best. However, cells made with 10% to 15% acetylene black will have voluminous cathodes in comparison to a cell made with 5%. Hence, depending upon the end application, the percentage of acetylene black can be judiciously selected. If a highly compact cell is required, a lower percentage of acetylene black may be preferred at the cost of some 8 to 10% reduction in the material utilization.

Conclusion

The magnesium–mercurous chloride battery system, unlike several other primary batteries, is capable of being continuously discharged at fairly high current rates. This battery falls within the category of high energy density batteries.

The magnesium–mercurous chloride battery shows an open circuit voltage of 1.65 V and a discharge voltage between 1.55 to 1.2 V at the 10 hour discharge rate. It can be drained at a current density up to 90 mA/cm^2 with perchlorate electrolyte and up to 75 mA/cm^2 with sodium chloride electrolyte. Because of its fairly high operational cell voltage and high current discharge capability, the magnesium–mercurous chloride heavy duty battery system has an advantage over many other primary cell systems.

The authors thank the Director, Central Electrochemical Research Institute, Karaikudi for his kind interest in the work.

1 M. J. H. Lemmon and W. E. Casson, Int. Symp. on Batteries, Signal Res. & Dev. Est., (UK), Paper J, (1958)
2 J. B. Mullen and L. P. Howard, Trans. Electrochem. Soc., 90 (1946) 529.
3 L. E. Pucher, J. Electrochem. Soc., 99 (1952) 203C - 204C.
4 Electrotechnika, 12 (1969) 50 - 52.
5 J. R. Coleman, J. Appl. Electrochem., 1 (1) (1971) 65 - 71.
6 K. Dakshinamurthi and P. B. Mathur, 12th Semin. Electrochem., Karaikudi, (1972).
7 R. H. Williams, Extended Abstract, The Electrochemical Society, 73-2 (1973) 19.
8 A. Fishback and H. J. Mandel, U.S.Pat. Appln No. 727, 005.
9 M. Margalit, Extended Abstract, The Electrochemical Society, 73-2 (1973) 105.
10 K. V. Prasad, N. Venkatakrishnan and P. B. Mathur, Indian Pat. No.1479/CAL/1974.
11 P. B. Mathur, K. Dakshinamurthi, R. Balasubramanian and P. N. Narayanan Nambooodiri, Indian Pat. No. 113, 763.