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Electrochemistry

ADVANCES IN BATTERY TECHNOLOGY—RESERVE BATTERIES

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The concept of activated batteries emerged during late 40s gave momentum to the use of magnesium alloy anodes in primary batteries in place of zinc. Although half cell potential and ampere hour output per unit weight of magnesium are much higher than zinc, its corrossion behaviour in most of the electrolytes could not prove this metal anode as a suitable substitute for zinc in primary dry cells. However, corrodibility of anode is of less importance in single shot reserve batteries and so magnesium could find an edge over zinc batteries in reserve battery field.

Noting wide utility of activated batteries, CECRI carried out extensive work on Magnesium activated batteries and explored a number of new systems, besides developing the conventional systems for meeting indigenous needs. Among the new systems investigated by Mathur and coworkers at the Institute, are Magnesium-Silver sulphate, Magnesium-Mercuric sulphate, Magnesium-Copper sulphate, Magnesium-Mercurous chloride, Magnesium-Lead chloride, Magnesium-Leaddioxide, electrolyte activated batteries. Results of investigations on these cell systems were already published separately. In this present paper, the performance characteristics and operational data of these cell systems are reviewed and compared with one another. This paper also includes the information on Tin-Silver oxide battery, which is a system developed at the Institute as an alkaline battery.

Keywords : Battery Technology; Reserve Batteries; Battery Systems

INTRODUCTION

SOME of the limitations of conventional batteries like low shelf life, failure to discharge at high rates and poor low temperature performance in the case of dry cells (Leclanche), large maintenance and poor energy density of lead acid battery and high cost, low energy density besides maintenance in the case of nickel cadmium and nickel iron secondary batteries, lent great emphasis on the development of new systems of reserve batteries also known as activated or single shot batteries for multitudes of new requirements cropped up with the advancement of new technologies during the last three decades.

Long shelf life, fast activation, high specific energy, high specific power, freedom from maintenance, good performance at extreme temperatures and mechanical ruggedness are some of the basic requirements of portable power sources needed for a large number of modern appliances. Neither all of these characteristics are

available together in a single battery system nor they are required for a specific application. For instance, rocketary needs a battery capable of extremely fast activation—of the order of a fraction of a second and possessing high specific energy and high specific power, radiosonde and other meteorological equipments need a battery of delayed time of activation of the order of 15 to 20 minutes besides high energy density and capability to operate at extremely low temperatures of the order of −60 to −80 °C. Navy needs batteries for life saving equipment and weaponry which should be capable of activation within a few seconds and which should possess high energy and high power density. In most of such applications, the energy is required for a limited period from a few seconds to several hours.

New Cell Systems Developed at CECRI

Noting a vast gap existing between the demand for specific power sources and their availability, the author along with his associates explored and developed a number of magnesium, zinc and other reserve battery systems during the last two decades. Some of these batteries can be adopted as dry or wet battery systems also.

Several of the sparingly soluble and fairly soluble compounds such as silver sulphate, copper sulphate, mercuric sulphate, mercurous chloride, lead dioxide, lead chloride, silver oxide, oxygen and organic nitrocompounds, whic are capable of being reduced cathodically, were coupled with magnesium, zinc and other anodes. Aluminium electrode was also explored in some cases but the cell voltage characteristics of aluminium cells is found to be poor. These investigations led to the development of a series of new battery systems notable among them are the following :—

1. Magnesium-silver sulphate battery (Lakshminarayanan *et al.*, 1974).
2. Magnesium-copper sulphate battery (Mathur & Paul, 1962, 1964).
3. Magnesium-mercuric sulphate battery (Prasad *et al.*, 1976/77).
4. Magnesium-mercurous chloride battery (Prasad *et al.*, 1976/77).
5. Magnesium-lead chloride battery (Dakshinamurthi & Mathur, 1972).
6. Magnesium-lead dioxide battery (Prasad & Mathur, 1976).
7. Tin-silver oxide battery (Mathur & Venkatakrishnan, 1972).
8. Magnesium-silver oxide aqueous (Mathur, 1966) and non-aqueous (Gangadharan *et al.*, 1977) batteries.
9. Magnesium-air cell (Mathur & Muniyandi, 1974)-Patent.
10. Zinc-alkaline organic cells (Balasubramanian *et al.* — *under preparation*).

Some of the important characteristics of the above listed first seven cells are surveyed in this paper. Some of the areas of applications of these new reserve battery systems are also indicated in the light of respective features possessed by them. Each one of these battery systems can be expected to acquire specific areas of applications as each one possesses different characteristics.

Operational Data and Discussions

The performance characteristics data of the first seven cell systems listed above are summarised in Table I, in respect of open circuit voltages, close circuit voltages, peak currents, cathodic efficiencies and percentage of acetylene black necessary in cathode mix for obtaining maximum efficiencies. Some thirty figures are presented in the paper. These figures relate to voltage *vs.* current, voltage *vs.* time characteristics of different cell systems and also depict cathodic efficiencies *vs.* concentrations of acetylene black in cathodes or cathodic efficiency *vs.* current drain. Voltage *vs.* current curves for the discharge of these cells, are presented in Fig. 1.

Table I

Some characteristics of new reserve battery systems

Cell System	Electrolyte	Open circuit voltage (volts)	Close circuit voltage (Volts)	Peak current density mA/cm²	Cathode efficiency (%)	Concentration of acetylene black at maximum efficiency (%)
1	2	3	4	5	6	7
1. Magnesium-Silver Sulphate	Magnesium Perchlorate + Sodium Chloride or Sodium Sulphate + Sodium Chromate	1.95	1.9–1.5	95 at 1.4V	75–85	30
2. Magnesium-Copper Sulphate	Copper Sulphate	1.6	1.5–1.0	150	45–60	—
3. Magnesium-Mercuric Sulphate	Magnesium Perchlorate or Sodium Chloride	1.9	1.8–1.3	90	75–85	35–40
4. Magnesium-Mercurous Chloride	Magnesium Perchlorate or Sodium Chloride	1.65	1.55–1.2	90 at 0.8V 75 at 0.875V	93–94	10–15
5. Magnesium-Lead Chloride	Sodium Chloride	1.1	1.0–0.8	70	60–90	—
6. Magnesium-Lead Dioxide	Sodium Chloride or Magnesium Perchlorate	1.9	1.75–1.2	70	60	5
7. Tin-Silver Oxide	Alkali (KOH)	1.5	1.45–1.0 (1.2V flat voltage)	480	75–85	—

It may be noted from Fig. 1 that different cell systems operate at fairly different potential-current levels. Magnesium-silver sulphate cell curve occupies the highest

positions in the figure, indicating highest cell voltages at all different current densities. Next high potential plateau system in the figure. is Magnesium-mercuric sulphate battery; others which follow them in sequence are: Magnesium-mercurous chloride, Magnesium-lead dioxide and lastly Magnesium-lead chloride battery system. While Magnesium-silver sulphate battery operates at as high a potential level as 1.9–1.5V, the last cell system Magnesium-lead chloride discharges between 1.05–0.08V.

With regard to the mechanical ruggedness and reliability, Magnesium-lead chloride cell system stands first among all these battery systems. Next come Magnesium-mercurous chloride, Magnesium-mercuric sulphate, Tin-silver oxide, Magnesium-silver sulphate and Magnesium-lead dioxide batteries.

From Table I, it may be noted that the discharge current density falls from system to system in the following order: Tin-silver oxide (480mA/cm^2), Magnesium-copper sulphate, Magnesium-silver sulphate, Magnesium-mercuric sulphate, Magnesium-mercurous chloride, Magnesium-lead chloride and Magnesium-lead dioxide.

Cathodic efficiency is observed to lie within the range of 45–90 per cent. Maximum efficiency is being exhibited by silver sulphate and mercurous chloride batteries, next best by Magnesium-mercuric sulphate and Tin-silver oxide batteries, cathodic efficiencies are somewhat lower in other cases.

Cells made with silver sulphate cathode coupled with different metal anodes like magnesium, zinc and aluminium have been compared in respect of their voltage

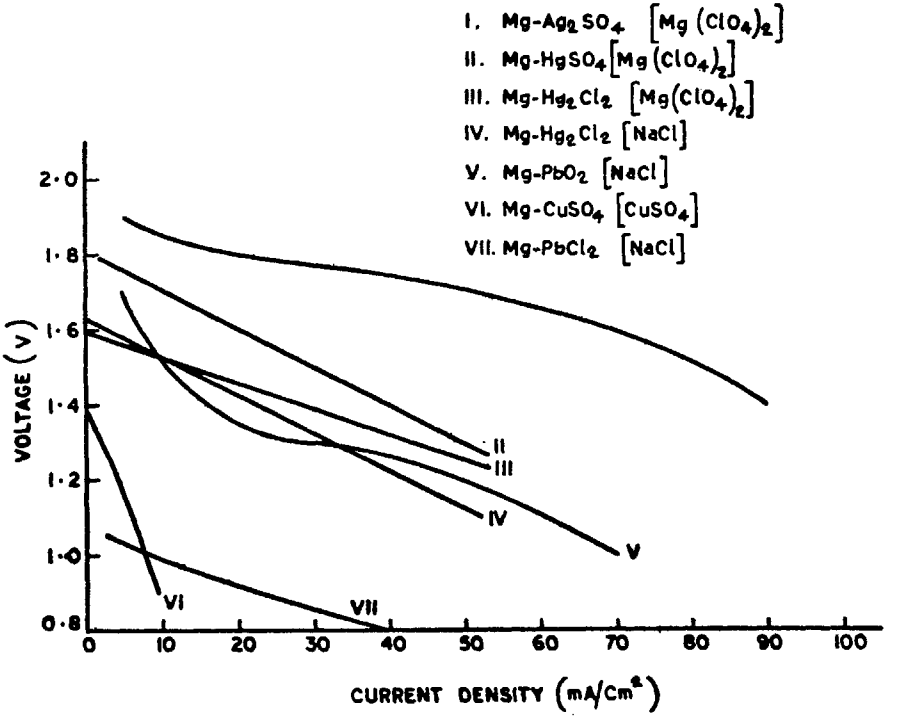

FIG. 1.

current characteristics. It may be noted from the figure that magnesium cell operates at the highest potential plateau. Zinc comes next and aluminium cell operates at the lowest voltage level.

Coupling the high energy density magnesium and silver oxide electrodes, the author developed Magnesium-silver oxide battery (Mathur, 1966) systems, wherein aqueous magnesium perchlorate or sodium chloride or mixtures of alkaline and neutral salts is used as the electrolyte. The system exhibits a high voltage of 1.9V. The author along with his associates later developed a nonaqueous magnesium-silver oxide battery system (Gangadharan *et al.*, 1977) in which a solution consisting of magnesium perchlorate in propylene carbonate is used as the electrolyte. The cell system operates between 2.0V to 1.2V within a low current density range of 0–4mA/cm^2. The cell system is useful as a voltage source at extremely low current drains for long duration applications.

From the data presented in the paper, it may be noted that the short duration requirements of high power and energy density battery systems can be best met with magnesium-silver sulphate, tin-silver oxide and magnesium-mercuric sulphate batteries, provided the cost is not a consideration. Requirements of high energy density battery for long duration use at fairly low cost can be best met with magnesium-lead dioxide, magnesium-lead chloride and magnesium-copper sulphate batteries. These later systems can be suitable for emergency lights and multitudes of other civilian and defence requirements.

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Discussion

V. S. BAGOTSKY (*The Institute of Electrochemistry of the Academy of Sciences of USSR, Moscow*) : How do you compare the activities of silver oxide and silver chloride electrodes, for instance, silver chloride is more active ?

P. B. MATHUR : Batteries incorporating silver oxide electrode, such as zinc-silver oxide and tin-silver oxide batteries, get activated in alkaline electrolytes in less than a second's time while magnesium-silver chloride batteries usually take 2 to 6 seconds for activation. Delay in activation is largely due to the magnesium electrode in magnesium/silver chloride battery.

V. S. BAGOTSKY : How do you compare silver chloride and lead chloride batteries ?

P. B. MATHUR : Both magnesium-silver chloride and magnesium-lead chloride batteries are sturdy, rugged and hence possess long shelf life of several years under dry conditions. Silver chloride battery possess nearly 1.5 times larger cell voltage than the lead chloride battery. Electrodes in both the cases are non fragile. Both the batteries can possess almost equal specific energies per unit weight. Both batteries can be activated with sea water. Materialwise magnesium/lead chloride battery is nearly 300 times cheaper than magnesium silver chloride battery.

V. S. BAGOTSKY : What are the comparative performances of silver oxide and silver chloride batteries and of magnesium/silver sulphate and magnesium/cuprous chloride batteries ?

P. B. MATHUR : In the present paper, I have described only tin-silver oxide battery which involves silver oxide cathode. Hence, I shall compare here some of the characteristics of this battery system with magnesium/silver chloride battery system in the first instance. Tin/silver oxide battery discharges for 80 per cent of its capacity at about 1.2–1.3V and 1.3–1.45V. But the most important feature of tin battery is its extremely high power output capability, viz., nearly 500 mA/cm^2 whereas magnesium/silver chloride cell has lower power output per unit area of the electrodes owing to the limitations of the conductivity of the electrolyte, viz., sea water which is generally used in the chloride battery systems. Second important feature of tin/silver oxide battery is its very low time of activation viz., less than a second.

Regarding comparison of magnesium/silver sulphate and magnesium/cuprous chloride batteries, the former is very much superior to the latter with regard to operational voltage and power output. Silver sulphate battery operates at as high a potential level as 1.9–1.6V whereas Magnesium/cuprous chloride battery operates between 1.35–1.1V. Cuprous chloride is less stable than silver sulphate and hence the shelf life of silver sulphate battery is better than that of cuprous chloride battery. Power output of silver sulphate battery is higher than that of cuprous chloride battery.