SOME ASPECTS OF THE PERFORMANCE OF THE SILVER ZINC SECONDARY BATTERIES*

C. G. SUBRAMANYAN, P. K. SAHA AND B. R. V. RAO

(*Received* 14 *May*, 65; *revised* 21 *Oct.*, 65)

A solution of some of the problems of the Silver-Zinc Cells, when used as a multiple cell battery, has been obtained and applied successfully to a typical 12V, 20 Ah Silver-Zinc multiple cell battery used to power a portable Military communication equipment.

Current trends of development on the optimisation of the performance of Silver-Zinc secondary battery system has also been discussed.

The silver-zinc secondary cell has possibly the highest energy density among the various secondary cells and is finding increasing applications in the field of electronics, especially in military systems. Although hardly any difficulty is experienced in charging a single cell battery to its full capacity, considerable charging problems are faced when a number of cells are used to form a battery. This is further aggravated when charging of the multiple cell battery has to be carried out in field areas, where facilities are generally inadequate. Similarly, during discharge of battery, while powering portable communication equipments in field areas there is a risk of individual cells reversing in polarity and getting damaged permanently due to low internal resistance and dissimilar discharge pattern of the cells. Investigations were undertaken to determine the most suitable method of charging and discharging these cells when used in a series connected battery configuration.

CHARGE AND DISCHARGE CHARACTERISTICS

The electro-chemical reaction of a fully formed cell can be expressed as follows :

$$\underset{\text{Discharged}}{Ag + Zn(OH)_2} \rightleftharpoons \underset{\text{Charged}}{AgO + Zn + H_2O}$$

During the charge cycle, the positive plate is first oxidised to silver oxide and finally to silver peroxide. On discharge the silver peroxide is reduced first to silver oxide and then to silver. This gives the cell the two-step characteristic at low and intermediate rates of charge and discharge which is typical of the silver-zinc accumulator. Fig. 1 gives the two-step charge/discharge characteristics of an individual silver-zinc cell at 10 hour rate. In the charging curve the first step just above 1·6V lasts upto a third of the total charge period. There is a sudden rise to a short peak at about 1·95V followed

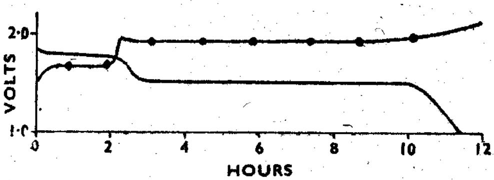

Fig. 1—Typical charge and discharge characteristics for a type HI0S accumulator.

*Paper presented by Shri P. K. Saha at the 5th Seminar on Electro-chemistry held on 30 January 1965 at CECRI, Karaikudi.

by a long step at 1·93—1·96V which is known as the 'peroxide stage'. The voltage is reasonably constant at this level until the charge is nearly completed when the voltage rises fairly steeply to 2·1V, measured whilst the cell is still on charge. Irrespective of the current at which the cells are being charged, the charge should always be terminated at 2·1V. Overcharging of a cell will lead to the electrolysis of the electrolyte and consequent loss of water. No increase in capacity is obtained as the thin plate system ensures complete conversion of active material without overcharge. Similarly in the discharge characteristics the first step which is around 1·8V lasts upto one-third of total discharge period and is followed by a longer and very flat stage between 1·5 and 1·55V. The actual voltage depends on the rate of discharge and the type of cell. The fall-off voltage from higher step to the lower and the final fall-off in voltage at the end of discharge is very rapid. For this reason, safe operation and maximum cell life, it is advisable to terminate the discharge of a cell when the terminal voltage falls to 1·0V. At very high discharge rates the cell temperature rises rapidly and the heat generated may damage the cell before full capacity is realised.

PROBLEMS OF SERIES CONNECTED CELL SYSTEM

The following are the main problems faced when a number of silver-zinc cells are used to form a battery :—

(*a*) A single cell can be charged at 10 hours rate to the full capacity when the cell, picks up an on-charge voltage of 2·1V. But when a multi-cell battery is charged at the same rate, all cells do not pick up charge in the same length of time. Hence it is very difficult to find out when the battery has attained full charge even under ideal laboratory conditions. There is thus a danger of overcharging individual cells in the battery.

(*b*) When a battery is being discharged, all the cells do not lose charge in the same length of time. One or more cells may get discharged earlier than others. There is thus a great chance of reversal of polarity of individual cells. This is particularly so, when the battery is discharged at a high rate. If this happens one or more cells may get distorted due to overheating and become unsuitable for subsequent use.

Fig. 2 and 3 illustrate the charge/discharge pattern of two similar types of 20 Ah silver-zinc cells connected in series.

Fig. 2 shows the initial charging characteristic at 20 hrs rate (*i.e.* at 1 amp). It would be seen that although cell No. 1 had attained 2. 1V after an input of 12 Ah, yet cell No. 2 was not fully charged. Hence the first cell was removed from the charging circuit and the second cell was charged till 2·1 V was reached. Input of 17Ah was required to get it fully charged.

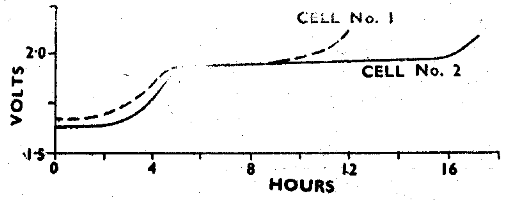

Fig. 2—Initial charging characteristics of 2 cell battery at 20 Hr. rate type H20S Ag-Zn cells.

Fig. 3 shows the 7th cycle discharge characteristics of this battery at 2 amps. It may be mentioned here that at the end of 6th discharge of the battery, the charging of the 7th cycle was continued at 2 amps till an input of 18·5 Ah was given when it was noticed that cell No. 1 had attained 2.1V and cell No. 2 was not fully charged. As individual monitoring of cells was not practised deliberately in this case, the battery was taken out of charging circuit and was allowed to discharge at 2 amperes when it was noticed (Fig. 3) that at the end of 7¼ hrs, cell No. 2 had been reversed in polarity while cell No. 1 was still strong. Hence Fig. 2 and 3 only illustrate that complete charge/discharge can be achieved only if the cells are tackled individually. Difficulty in charging and discharging is always present if more than one cell is used to make a battery. More difficulty is experienced if more cells are in series. This dissimilar charge/discharge pattern of individual cells can be improved to a certain extent by careful selection of cells (from the same batch and date of manufacture), but there is always need for careful control and supervision, while charging/discharging series connected silver-zinc cells, without which it is not possible to utilise fully the rated Ah capacity of the cell and take advantage of the high energy density of the silver-zinc system.

This method of charging and discharging a battery by monitoring individual cells is definitely cumbersome and not practicable if the battery is required for use in field areas for military applications. Hence a further modification of the charging and discharging procedures to suit the field conditions is called for.

EXPERIMENTAL PROCEDURE

Investigations were carried out on a seven-cell series connected silver-zinc battery (12V 20Ah) required to power a ground-to-air VHF wireless communication set. The battery had the following specificational details :

(*i*) Seven 20Ah cells are connected in series to give a terminal voltage of 12V with a spare cell in it.

(*ii*) Size and weight 220 × 110 × 119 mm, 4 kg (including the outer container).

(*iii*) Battery is required to power a communication equipment for a minimum period of 4 hours continuously at the appropriate send/receive ratio before it requires to be recharged.

(*iv*) The current consumption of WS is 4·6 amperes while transmitting, 3·5 amperes while receiving.

(*v*) A send/receive ratio of 2 minutes to 10 minutes to an end point voltage of 9·6V is required to determine battery life.

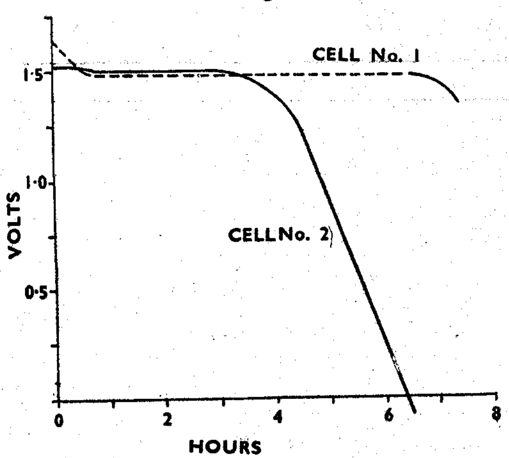

Fig. 3—7th Cycle discharge characteristics of 2 cell battery at 2·00 amperes type H 20S Ag-Zn cells.

The above battery was assembled using imported 20Ah cells of same date of manufacture to ensure proper matching. The battery was subjected to cyclic life tests of charge and discharge to the programme given below :

(i) *Initial charge and discharge cycles* (two cycles)—The initial charging was carried out at 20 hour rate till all the cells showed 2.1V. The discharge was conducted at 10 hour rate. The discharge was stopped when the terminal voltage of any one of the cells dropped to 1·4V. This was necessary so that electrodes of each cell could be fully formed.

TABLE 1

DISCHARGE PATTERN OF INDIVIDUAL CELLS (in Volts)

No. of Hours	Cycle No 10 Cells						
	1	2	3	4	5	6	7
0	1·78	1·78	1·78	1·78	1·78	1·78	1.78
1	1·70	1·70	1·70	1·70	1·70	1·70	1·70
2	1·49	1·49	1·49	1·49	1·49	1·50	1·49
3	1·48	1·49	1·49	1·48	1·48	1·49	1·49
4	1·43	1·46	1·49	1·44	1·46	1·47	1·43
4½	1·38	1·43	1·44	1·39	1·44	1·44	1·38
5							
5½							

No. of Hours	Cycle No 20 Cells						
	1	2	3	4	5	6	7
0	1·73	1·73	1·72	1·73	1·73	1·71	1·73
1	1·56	1·56	1·52	1·56	1·57	1·58	1·55
2	1·48	1·48	1·48	1·48	1·47	1·49	1·47
3	1·46	1·46	1·46	1·46	1·46	1·46	1·46
4	1·44	1·45	1·44	1·44	1·44	1·46	1·45
4½							
5	1·38	1·42	1·42	1·38	1·41	1·46	1·38
5½							

No. of Hours	Cycle No 30 Cells						
	1	2	3	4	5	6	7
0	1·74	1·74	1·72	1·74	1·74	1·72	1·68
1	1·47	1·47	1·47	1·47	1·47	1·48	1·47
2	1·47	1·47	1·47	1·47	1·47	1·48	1·47
3	1·46	1·47	1·47	1·47	1·47	1·48	1·47
4	1·44	1·44	1·44	1·43	1·44	1·46	1·44
4½							
5	1·41	1·42	1·42	1·41	1·42	1·43	1·40
5½							

TABLE 1—*contd*

No. of Hours	Cycle No 40 Cells						
	1	2	3	4	5	6	7
0	1·78	1·78	1·78	1·78	1·77	1·78	1·78
1	1·66	1·66	1·66	1·66	1·66	1·66	1·66
2	1·51	1·51	1·51	1·51	1·51	1·51	1·51
3	1·50	1·50	1·50	1·50	1·50	1·51	1·51
4	1·48	1·49	1·49	1·49	1·49	1·49	1·45
4½							
5	1·45	1·46	1·47	1·46	1·45	1·49	1·46
5½	1·40	1·44	1·45	1·45	1·43	1·43	1·43

No. of Hours	Cycle No 50 Cells						
	1	2	3	4	5	6	7
0	1·75	1·75	1·74	1·75	1·74	1·76	1·75
1	1·49	1·58	1·57	1·49	1·49	1·64	1·48
2	1·47	1·47	1·47	1·47	1·47	1·47	1·46
3	1·47	1·47	1·47	1·47	1·47	1·47	1·47
4	1·45	1·45	1·45	1·45	1·45	1·47	1·45
4½							
5	1·43	1·43	1·43	1·43	1·43	1·43	1·43
5½	1·39	1·42	1·42	1·40	1·41	1·41	1·41

(*ii*) *Charge cycle* (*subsequent*)—The battery was charged at the 10 hour rate (2 amps.) till the terminal voltage reached 14—14.7V. The charging was discontinued when one of the cells reached 2·1V. This ensured that no cell was overcharged although the battery as a whole might not be fully charged.

(*iii*) *Discharge cycle*—The battery was discharged through fixed load resistances to simulate the actual wireless set drain conditions *i.e.*, discharge through 2·61 ohms for 2 minutes and 3·43 ohms for 10 minutes continuously. The discharge of the battery was discontinued as soon as any one of the cells reached 1·4V. Thus discharge cycle ensured that no single cell in the battery configuration was driven below 1·4V which was a very safe limit to avoid the cell reversal. However, such a recourse limited full utilisation of the rated Ah capacity of the battery.

The duration of the discharge over a period of 50 cycles starting from the fifth cycle is given in Fig. 4. The discharge pattern of individual cells in the 10th, 30th and 50th cycles is given in Table 1. The average Ah input and output for the 50 cycles is given in Table 2. The trials were suspended after the 53rd cycle when one of the cells developed defects and became unserviceable.

DISCUSSION

The following salient points emerged from an analysis of the above results :

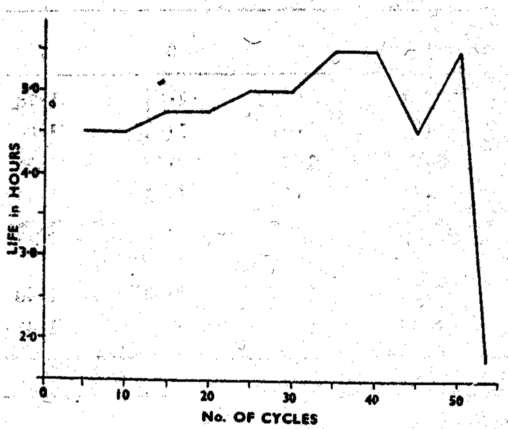

Fig. 4—Curves showing life in hrs. *vs* No. of cycles of Ag-Zn battery of 7H 20S cells.

(*a*) The 7-cell battery system could operate a wireless set for a minimum of 4 hours for a life span of 50 cycles.

(*b*) As the average input was only of the order of 18·3Ah, 91·5 percentage capacity of the battery was utilised. This naturally kept the end point voltage of the individual cell well above the danger limits for cell reversal.

(*c*) The charging of the battery could be carried out using a field charging set of the required capacity having facility to read charging currents and voltages accurately.

TABLE 2

INPUT/OUTPUT FOR EACH CYCLE UPTO CYCLE NO 53 WHEN ONE OF THE CELLS IN THE BATTERY FAILED

Cycle No.	Input (in Ah)	Output (in Ah)	Cycle No.	Input (in Ah)	Output (in Ah)	Cycle No.	Input (in Ah)	Output (in Ah)
1	22	14	19	18	16	37	20	18
2	23	16	20	17	16	38	19	19
3	16	12·5	21	17	16	39	18·5	18*
4	14.	12·5	22	19	16	40	18·5	18
5	12	12	23	18	16	41	18·5	18
6	16	13	24	17·5	16·5	42	16	13·5
7	14	13	25	19	16	43	19	16
8	14	13	26	18	16	44	16	16
9	14	13	27	16	16	45	16	15
10	15	15	28	16	16	46	16	16
11	18	16	29	18	16·5	47	15	15*
12	14	13	30	18	16	48	16	16
13	18	16·5	31	16	16	49	19	16·5
14	17	16·5	32	18	16	50	18	16·5
15	18	16	33	16	16*	51	19	15
16	16	15	34	17	17	52	17	16
17	16·5	15	35	17	16*	53	17	12
18	18	15	36	20	17			

(d) If a fully charged battery is used with a wireless set, no attention is required on it for a period of 4 hours.

(e) The cell to cell discharge pattern of the 7-cell battery throughout its 50 cycle life period was not varying appreciably from each other (± 80 mV). This is possibly due to the selection of cells of the same batch and date of manufacture.

(f) In view of para (e) and sufficiently high end point voltage limits for the WS performance ($9 \cdot 6 V = 7 \times 1 \cdot 375$), it is likely that no damage is bound to occur to the individual cell in the battery, if its recharging state is determined by the non-operation of the wireless set due to the battery voltage going down below the specified end-point voltage limits for the set. This method of "battery end of life determination" is most suitable and desirable in field areas. This, however, requires guarantee that the wireless set should cease to function satisfactorily below an input of 9·6V. (In this particular case, it has been indicated that the communication equipment will not function satisfactorily below an input of 9·6V).

MODIFIED CHARGE/DISCHARGE PROCEDURE FOR THE 12V 20Ah SILVER-ZINC BATTERY

As a result of experimental trials and deductions, a modified charge/discharge procedure for the 12V 20Ah silver-zinc battery in field areas is suggested as follows:—

Charging procedure—Equipments

(i) A field charging set capable of delivering the required voltage and current.

(ii) Built-in facility in the charging set to read charging currents upto 0·5 ampere.

(iii) A voltmeter reading upto 1/10th of a volt to check individual cell voltages.

Method of subsequent charging in field areas

The battery should be charged at the 10 hour rate till the terminal voltage while on charge is 14—14·7V. The charging should be discontinued if any of the cells reaches 2·1V, while on charge.

Discharge procedure

A fully charged battery should not be used with a wireless set for more than 4 hours when it should be taken out for recharging. If somehow it is not possible to do so, the battery should be taken for recharging as soon as the wireless set fails to operate satisfactorily.

The above modified method of charging and discharging will ensure a good cyclic life for the battery and will minimise individual cell failures. A further simplification of the charging procedure would be to investigate the suitability of constant potential charging in field roles. A suitable adapter to deliver a regulated constant charging voltage (say 2—2·1V per cell) could be used with conventional constant current field charging set. The cyclic life and the Ah output for the 7-cell 12V 20Ah battery system requires investigation under different constant potential charging voltage to arrive at optimum conditions.

DEVELOPMENT ON OPTIMISATION OF PERFORMANCE

The poor charge/discharge cyclic capability of silver-zinc battery system is still a major problem faced by battery technologists everywhere. Two major objectives of current battery research programmes regarding silver-zinc battery are longer life and

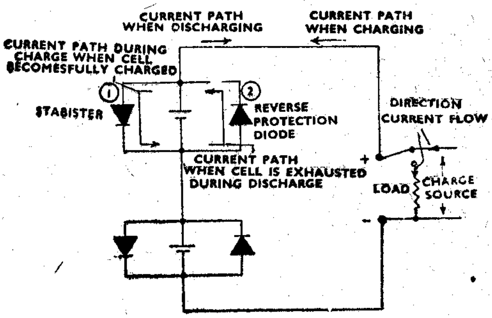

Fig. 5—Stabistor operating circuit used with a nickel—cadmium battery.

more watt hours per lb. A recent paper shows the use of stabistor diode, which is a semi-conductor connected across each cell, to prevent overcharge and cell reversal. It is claimed that this system will greatly prolong the life of silver-zinc battery by preventing over-heating and failure of individual cells and consequent failure of the whole battery. In this case, a weak cell would be permitted to loaf along until it recuperated, while the rest of the cells carried the load. Fig. 5 shows the essentials of the stabistor operating circuit used with a nickel-cadmium battery for space application. 'A' is a stabistor diode with a well-ordered forward conduction knee and a low dynamic impedance. As soon as the cell voltage reaches 1·45V at 70°F, the stabistor prevents current from flowing into it while under charge. 'B' is a second germanium type diode with lowest possible forward voltage break-over, connected across each cell with the polarity arranged so that this diode is biased off when the cell terminal voltage is nominal. If the voltage of the cell goes to 0·3 volts the diode proceeds to conduct current around the battery cell thus preventing the cell's reversal of polarity.

In the above system cell performs well, provided it is kept constantly cycling from charge to discharge. If the charge is interrupted, the stabistor diode has a relatively high back leakage which would tend to discharge the cell over a short period of time. This tends to limit other application of the stabistor system at this time until stabistors with a low back leakage are developed. Unless better and economical methods are available, solution to the present problem has to be worked out on individual cases depending upon particular application after actual trials as has been suggested for 12V 20Ah battery system in the specific role of operating a communication equipment. This is only a temporary solution to the problem as it suffers from slightly poor utilisation of the available energy in a silver-zinc battery. A permanent solution would be to develop a silver-zinc battery to deliver its full rated energy densities without appreciable suffering in its cyclic life under field usage conditions.

REFERENCES

1. FARMERY, H. K. & SMITH, W.A., "Some Material Problems of Silver Zinc Secondary Battery". 3rd International Symposium on Batteries (Pergamon Press Ltd., London), 1963.

2. "Venner Light Weight Accumulator—Technical Manual VA 60" (Venner Accumulators Ltd., England).

3. "Catalogue Venner Light Weight Silver-Zinc Accumulator" (Venner Accumulators Ltd., England).

4. BOOTH, E. M., "Constant Potential Charging of Small Accumulators—60" (Signal Research and Development Establishment, England), 1960.

5. YAFFEE, MICHAEL, L., *Aviation Week Space Technol.*, **80** (1964), 51.

6. "Pamphlet on New Battery Development Rechargeable Nickel Cadmium Battery Stabistor System" (Sonotona Corporation, U.S.A.).

7. KERALLA, J. A. & LANDER, J.J., "Sealed Zinc Silver Oxide Batteries", (PSC Publication Committee Red. Bank U.S.A.), May 1962, p. 105.

8. LANDER, J. J. "Sealed Zinc Silver Oxide Batteries" (PSC Publication Committee, Red Bank U.S.A.) 1961, p. 17.