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EXPERIMENTAL STUDY OF SIX INTERCONNECTED SODIUM/SULPHUR CELLS*

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Summary

A small battery of six interconnected Na/S cells has been operated for 1.5 years, having a total cycle life of 1325 cycles. Studies of electrical performance and behaviour under various normal and abnormal operating conditions have been undertaken. The results can be used in conjunction with theoretical data, in order to provide one of many important inputs into the optimum battery design for any particular application.

Introduction

It is generally accepted that in a practical sodium/sulphur battery cells will have to be interconnected in order to provide an adequate specific energy for a practical battery. For any particular application, a minimum number of series connected cells (*Ns*) are required to meet voltage demands; also a minimum number of such series chains are required (*Np*) in order to provide specific power capabilities.

By way of example, Fig. 1 shows a hypothetical 96 cell battery (where $Ns = 12$ and $Np = 8$) having the minimum number of inter-cell connections necessary to complete the battery. If every cell behaved in an ideal manner, the performance of this battery would be insensitive to additional parallel connections. However, it is known that practical cells never perform ideally, consequently the relationship between cell performance and inter-cell parallel connections has to be considered carefully.

Relevant cell characteristics are: (i) the internal resistance of a Na/S cell increases rapidly on overcharge; (ii) finite capacity loss occurs on cycling; (iii) extreme cell failure can occur leading to either an open circuit or short circuit cell.

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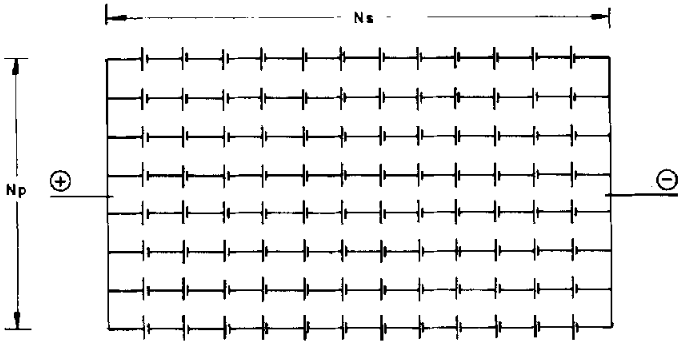

Fig. 1. Sodium/sulphur battery of 96 cells in an 8 × 12 cell array ($OCV \sim$ 25 V) $ns = Ns = 12$.

The presence of a high resistance cell in a series chain limits current flow through itself, and all cells in series with it, giving an amplified effect of a single cell malfunction. On this basis, if such a cell behaviour is expected frequently, one can argue that long series chains of cells in a battery design are undesirable.

At the other extreme, if all cells were series and parallel connected, a short circuited cell would lead to overdischarge, probably at high currents, of all cells in parallel with it. This would lead to total battery failure.

It was the purpose of this experimental study to examine the electrical behaviour of sodium/sulphur cells when interconnected both under normal and faulty cell conditions. The programme was regarded as complementary to theoretical predictions of battery performance under all conceivable conditions, and as an extension to earlier work by Minck [1] of the Ford Motor Co.

Experimental

As a first step, it was decided to build a small battery of six similar Na/S cells of a reliable proven design. With six cells, only two possible series/parallel connected matrices are possible, namely 3 parallel lines of 2 cells in a series (3 × 2 array, $ns = 2$) and 2 parallel lines of 3 cells in a series (2 × 3 array, $ns = 3$), where ns = the number of series cells between parallel links. (In this case $ns = Ns$ but in larger batteries multiples of ns may aggregate to give the total number of cells in series Ns.)

The cell

The cell chosen for this particular experiment is shown in Fig. 2. It had a central cathode (sulphur electrode contained within the electrolyte tube) and a gravity fed outer sodium electrode. Cell closure was achieved by Grafoil gasketed compression seals. The operating temperature of all cells was 350 °C.

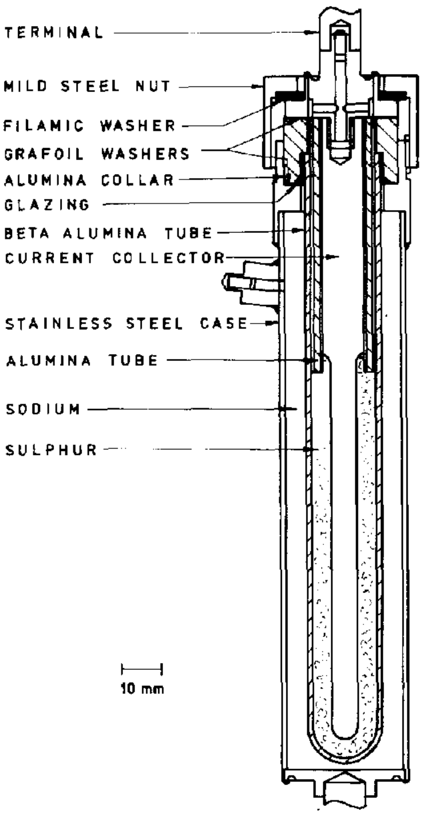

Fig. 2. Central cathode Na/S cell.

The nominal sulphur limited capacity of each cell was 20 Ah. In practice at a discharge rate of 100 mA/cm^2 to an *OCV* of 1.78 V and a charge rate of 50 mA/cm^2 to an operating voltage of 3.0 V, the actual reversible capacity of the cells initially was 15 ± 0.5 Ah. The β-Al_2O_3 electrolyte was supplied by Chloride Silent Power Ltd., Runcorn, U.K. The internal resistance of the cells was 0.034 ± 0.001 Ω, measured on discharge at *OCV* of 1.90 V.

The battery — normal operation

The cells were operated at 350 °C within a steel protective housing. Heavy duty copper bus-bars were used to connect the cell terminals to a multi-terminal insulating board. The individual cell voltages were monitored close to the cells and recorded continuously. Each cell was cycled once in isolation prior to making any inter-cell connections.

When all cells were fully charged the cells were connected into a 2 × 3 array for running as a battery. The choice of limits for the battery charge and discharge cycles, as with cells, are rather arbitrary. It was decided to discharge the battery at a constant current of 15 A (100 mA/cm^2) until one

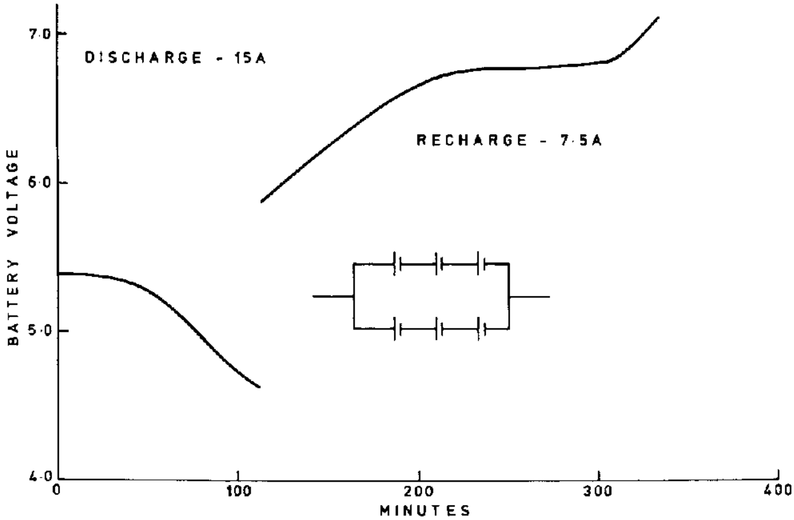

Fig. 3. Battery voltage curves for 2 × 3 cell array (cycle 1 - 47).

TABLE 1

OCV of individual cells after isolation at end of discharge

Time after isolation	Cell number					
	8	5	2	10	4	3
< 20 s	1.820	1.808	1.815	1.821	1.804	1.791
6 min	1.837	1.827	1.828	1.836	1.818	1.804

of the cells had reached an *OCV* of 1.78 V. (It was necessary to break the parallel connections momentarily in order to obtain a true reading for any cell.) The operating voltage at this point was defined as the end of discharge. Recharge was carried out at 50 mA/cm^2 until one cell reached an *operating voltage* of 3.0 V, this point being defined as the fully charged state.

The initial discharge was carried out (Fig. 3) and at the end point the *OCV* of each cell was measured (a) immediately and (b) after 6 min.

The readings shown in Table 1 give both a measure of the relative state of charge of each cell and also an indication of the degree of polarization incurred. The initial value of the *OCV* of cells at termination of discharge was used throughout the experiments as a guide to the relative state of charge of the cells on cycling. The associated recharge curve at 7.5 A is also shown in Fig. 3.

The practical battery capacity was 27.5 Ah (cf. the calculated capacity of ~ 30 Ah based on an average cell operating capacity of 15 Ah). This represents a 143 Wh battery, taking the average discharge voltage as 5.2 V.

The power obtained varied from 81 W initially to 69 W. The battery was then cycled continuously for a further 47 cycles. The voltage curves were superimposable for each cycle indicating no apparent deviation of battery performance.

A seal electronic short circuit developed in one of the cells at this point, the effect of which is discussed later. A similar replacement cell was utilized and the cells reconnected into a 3 × 2 array. The battery was cycled under the same current density conditions as the previous array (now 22.5 A discharge and 11.25 A charge). The voltage curves obtained are shown in Fig. 4.

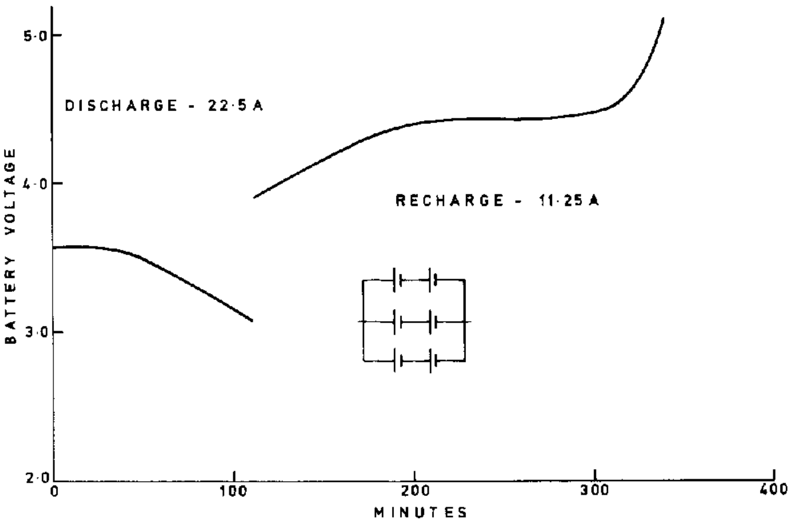

Fig. 4. Battery voltage curves for 3 × 2 cell array (cycle 1 - 119).

The capacity for this initial discharge was 41.6 Ah and the recharge capacity was 40.87 Ah (cf. 45 Ah if average cell capacity = 15 Ah). The initial capacity was therefore ~ 92% of that expected from the performance of single cells. The power during discharge varied from 80.55 W to 68.62 W. The battery was then automatically cycled over a 30 Ah cycle at 16.4 A discharge and 7.2 A charge. Periodically a full cycle was carried out to determine the battery capacity and to monitor the individual cell *OCV* at end of discharge. 119 cycles were completed without any detectable change in capacity. The voltage curves for these cycles up to 119 were superimposable on that of cycle 1. Very little fluctuation in the "end of discharge" *OCV*'s was monitored as shown in Table 2.

After cycle 120, there was a detectable deviation both in these values and in the battery capacity on subsequent cycling. The *OCV* data at the end of discharge for the following 15 cycles are shown in Fig. 5 where it can be seen that there was an overall decrease in the *OCV* of cell 8, until it reached 1.75 V and then it remained constant. At the same time the value for cell 10 (which is in series with cell 8) increases markedly. The remaining 4 cells show

TABLE 2

Instantaneous *OCV*'s for individual cells at end of discharge

Cycle	Cell number						Battery capacity (Ah)
	8	15	2	10	4	14	
1	1.800	1.801	1.785	1.821	1.783	1.843	40.87
18	1.802	1.803	1.790	1.825	1.793	1.837	
50	1.801	1.810	1.792	1.828	1.797	1.843	
78	1.800	1.802	1.787	1.825	1.794	1.834	
119	1.799	1.803	1.789	1.829	1.796	1.842	40.87

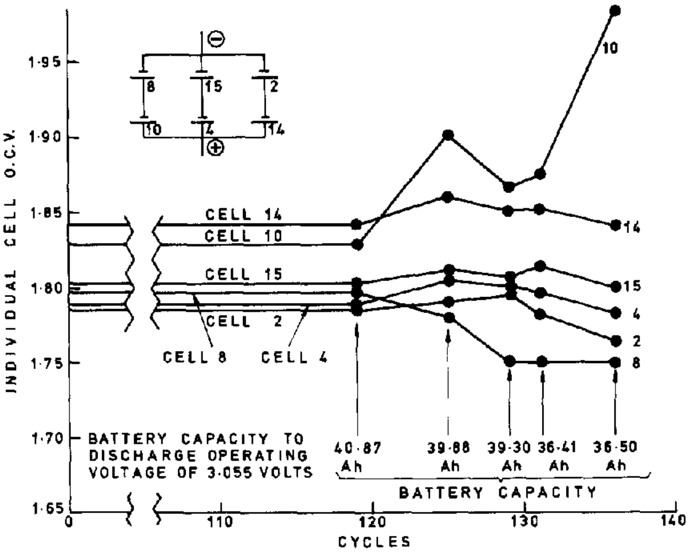

Fig. 5. Effect of slight electronic short circuit in one cell (8) on relative state of charge of cells at end of discharge.

lesser variations with an overall slight tendency towards discharge. The battery capacity figures are shown to decrease steadily from 40.87 to 36.5 Ah during this time if one fixes the discharge limit of the battery, as before, to be at an operating voltage of 3.055 V. If the original definition of limiting discharge to the point when the first cell reaches an *OCV* of 1.78 had been adhered to, then the battery capacity would have decreased even more rapidly.

This battery behaviour pointed to the fact that cell 8 was developing a slight electronic short circuit, and was itself slipping slowly towards discharge on cycling of the battery. In order to compensate for this lower voltage, its series partner (cell 10) gradually became less discharged in order to maintain the voltages of all 3 parallel chains identical. The result of this was that when the battery was charged, cell 10 reached full charge first and

TABLE 3

Instantaneous *OCV*'s for individual cells at end of discharge

Cycle	Cell number						Battery capacity (Ah)
	16	15	2	10	4	14	
1	1.901	1.780	1.799	1.825	1.803	1.829	25.1
125	1.884	1.792	1.794	1.809	1.809	1.820	25.0

more current was diverted to the other 2 chains. The overall effect was a decrease in capacity of the battery with the faulty cell never achieving the fully charged state. It was noteworthy that the *OCV* of this cell did not decrease below 1.75 V (greater than the 1.72–1.73 V normally associated with the Na_2S_2/Na_2S_3 two phase region). A replacement cell was substituted for the faulty cell and the original 2 × 3 cell array was reconstituted.

At this point in the experiment, the lowest capacity cell in each chain was 13.7 and 14.5 Ah (*i.e.* if both chains are utilized fully, 28.2 Ah should be available theoretically). In practice 25.1 Ah was obtained on the first cycle (89% practical availability) and 25.0 Ah after 125 cycles. This result confirmed the reproducible findings in the initial 2 × 3 array. Again Table 3 shows only slight variations in the relative *OCV* of individual cells. It has been demonstrated that both options for the interconnection of 6 cells have given a battery which has cycled under fixed constant current conditions for > 100 cycles without any significant capacity loss or deviations in relative states of charge between cells. It is concluded that there are no unforseen problems in cycling interconnected, similar cells.

It must be pointed out that in all of these battery experiments, the capacity actually obtained was ~ 90% of that expected based on the lowest capacity cell in each chain. This figure should be taken into account when desiging a battery to have a specific operating capacity. This percentage figure may in fact reduce slightly further when more cells are connected in series.

The battery — abnormal operation

The term abnormal operation signifies cycling of a battery deliberately having at least one cell or one environmental parameter different from those in the previous section.

Effect of a low capacity cell

In order to simulate the conditions of one cell suffering a loss of capacity, one of the cells in the 2 × 3 array was replaced by a cell (cell 18) which was malfunctioning to the extent of having a reversible capacity of 6 - 7 Ah compared to the other cells (13.5 ± 0.5 Ah at this stage). Cell 18 was of similar design to the existing cells except that it had a molybdenum cathode current collector which was polarizing prematurely on charge in the two phase region.

Under practical battery operation, the malfunctioning cell would lose capacity during normal cycling. When substituting a cell by another with about half its capacity there are two possible extreme situations for recommencing battery operation; *viz.*, either all cells start at the fully charged state or alternatively all cells start at the fully discharged state (*OCV* = 1.78 V). It was decided to investigate the behaviour of the battery under both of these extreme cases, but in reality the existing situation would be somewhere in between.

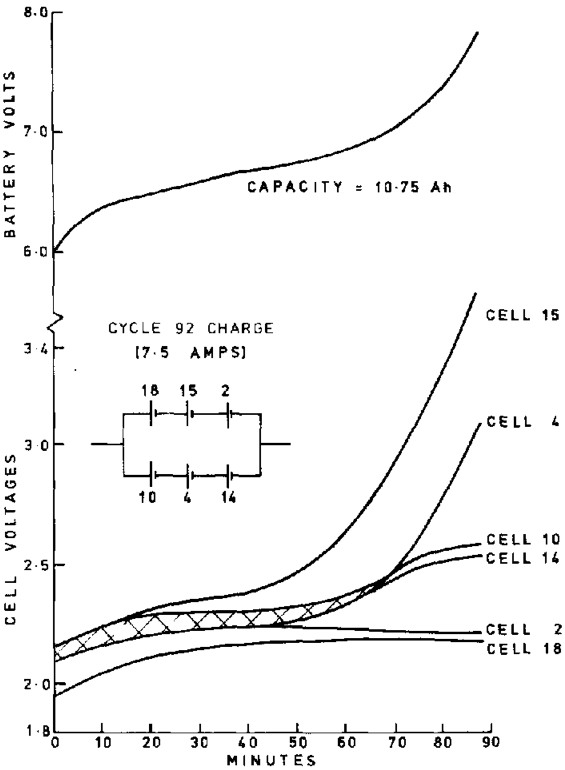

Fig. 6. Battery and cell voltages on charge when battery incorporated low capacity cell (18). (Initially all cells fully charged.)

All cells fully charged. The battery was subjected to 92 cycles between the fully charged state (operating voltage of 7.8 V) and the point at which the low capacity cell reached an *OCV* of 1.78 V. During this time the battery capacity only decreased from the low value of 12.0 to 10.75 Ah. The voltage curves for this battery and its cells are shown in Fig. 6. The measured capacity was insensitive to raising the upper voltage limit to 9.0 V, this only increasing the capacity to 12.5 Ah. The reason for such a low practical capacity was that 5 of the cells never discharged below an *OCV* of 1.87 V — the consistency of the capacity shows that the cells stayed in step under these conditions of operation.

Whilst the capacity was insensitive to an increase of the high voltage limit, a considerable increase was obtained by decreasing the low voltage limit to 4.5 V. A reversible capacity of 17.5 Ah was achieved with the weak cell reaching a stable *OCV* of 1.75 V on each cycle. This capacity was remarkably stable for 60 cycles showing that a cell of considerable reduced capacity can be carried in a battery and overdischarged during each cycle, without causing the cells to get out of step with regard to their relative state of charge.

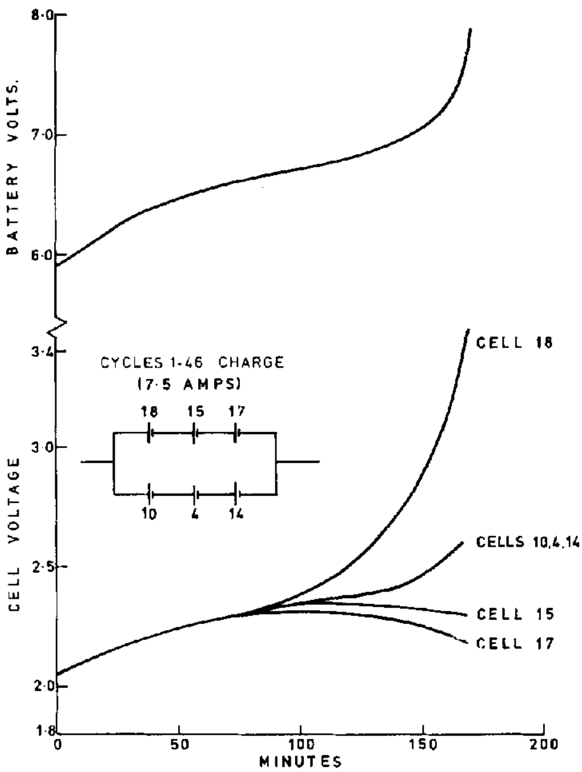

Fig. 7. Battery and cell voltages on charge when battery incorporated low capacity cell (18). (Initially all cells fully discharged.)

All cells fully discharged. The 6 cells were individually discharged to *OCV* of 1.78 V. The battery was charged at 7.5 A to a 7.8 V terminal voltage and then discharged at 15 A to 4.45 V cut-off voltage. The reversible capacity was 20.0 Ah, decreasing only to 19.1 Ah after a further 45 cycles. Both the obtained capacity and the monitored cell *OCV*'s at end of discharge showed that under these conditions most of the practical capacity of the cells was utilized. The voltage charge curves are shown in Fig. 7 for both battery and cell. Thus whilst the presence of a cell of reduced capacity can have a marked effect on the battery capacity, the actual quantitative extent of the reduction is critically dependent on the operating conditions imposed on the battery. Subsequent cycling does not appear to reduce the capacity drastically and the cells relative state of charge from cycle to cycle remain virtually unchanged.

Cell failure

The term cell failure embodies many abnormal events which can occur with a Na/S cell. A cell can suddenly lose its voltage and develop either a very high or low internal resistance. It is much easier to predict the effect on a battery of one cell failing to an open circuit condition as all current flow ceases through its series chain; consequently its effect on other cells is easily computed.

The situation is much more complicated if a cell fails to a short circuited (low resistance) condition. Two cases of sudden loss of cell voltage in a 2 × 3 array were observed during this experiment; on both occasions a low resistance cell resulted. The subsequent behaviour of the two batteries differed as the battery operation was being governed by different criteria.

In the first instance, the battery was 80% charged. Immediately the cell failed, an external monitoring device isolated the battery terminals to an open circuit condition. However, circulating current flowed within the battery; the two remaining cells in series with the failed cell were rapidly charged by the 3 cells in parallel until the voltage of the 2 series chains was equilibrated. At this point the circulating currents ceased and one of the 2 charged cells had assumed a stable over-voltage of ~ 4.0 V. The open circuit voltage of the battery at this point was 6.22 V, *i.e.* by measuring the battery *OCV* it was not possible to detect that one of the cells had failed. However, it was immediately obvious when cycling of the depleted battery was recommenced under the same constant current operating conditions. Little current was drawn from the depleted 2 cell chain. Throughout the discharge, the sum of the operating voltages of the 3 cells in the complete chain approached 4.14 V (the sum of the open circuit voltage of the 2 cell chain). Thus the depleted chain was maintained close to a fully charged state. This means that the effect of the short circuited cell on subsequent cycling of the battery in this particular arrangement, and under these operating conditions, approximates to that of an open circuited cell. The factors influencing this behaviour are easily computed. As the number of cells in a series chain, *ns*, increases and as the discharge current increases one reaches a point where the sum of the operating voltages of the complete chain is equal to and then less than 4.14 V whereupon some limited discharge of the cells in the depleted chain will be obtained. However, on the next recharge it can be shown by similar aggregate voltage considerations that the cells in the depleted chain will be charged preferentially at much higher current densities prior to the full series chain. Repeated high current charging is acknowledged to be an undesirable imposition on β-Al_2O_3 electrolyte leading to reduced life. Consequently if repeated cycling of a battery with a short circuited cell is considered to be a

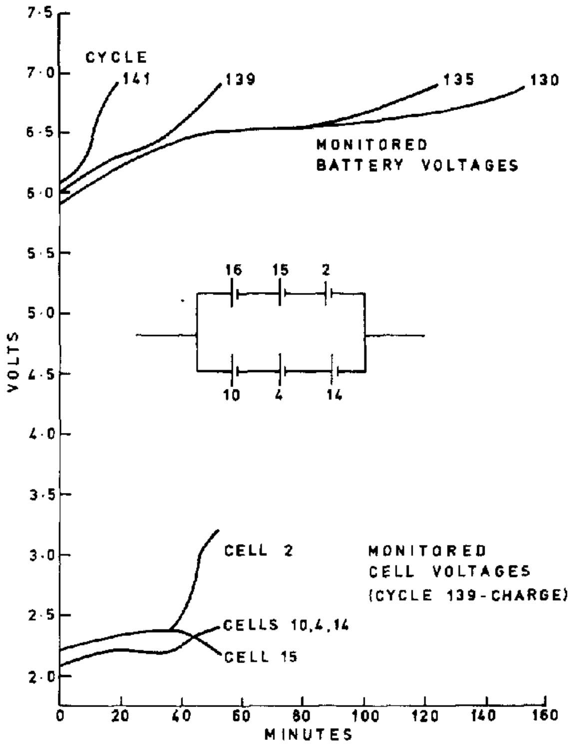

Fig. 8. Charge curves of constant current battery cycling between voltage limits after failure of cell 16.

frequent event then it could be advantageous to design the battery such that in the event of such a cell failure it behaves as if it were in an open circuit condition.

The other occurrence of sudden failure of a cell to short circuit occurred when the (2 × 3) battery was cycling continuously between fixed predetermined operating voltage limits. Figure 8 shows the effect such a failure had on the next 11 cycles of the battery charge voltage curves and individual cells after 9 cycles. It can be seen that a drastic loss in capacity occurred under these conditions due to the short circuited failure of cell 16. Cell 2, in series with 16, took about 12 cycles to reach a position where it remained fully charged permanently; the capacity of the battery was severely limited then by the effect of the imposed voltage limits on the complete series chain carrying twice the intended current.

Temperature effect

Cells No. 2 and 16 were replaced by other cells and the 2 × 3 cell battery (at 350 °C) operated for > 100 cycles under constant current conditions, between the two voltage limits of 4.6 and 9.0 V. The reversible

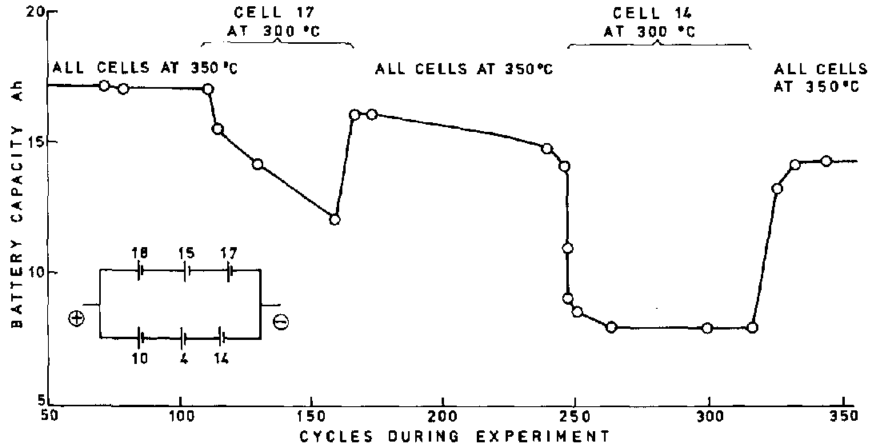

Fig. 9. Effect of variable cell temperature on battery capacity.

capacity was fairly constant at 17.2 Ah. The temperature of one of the new cells (17) was then reduced to 300 °C.

A rapid loss in battery capacity occurred with cell 17 limiting the charge acceptance. This immediate drop in capacity followed by a slower decrease in the subsequent 50 cycles is shown in Fig. 9. To see whether this was an irreversible loss in battery capacity the temperature of cell 17 was returned to 350 °C. Again from Fig. 9 it can be seen that most of the original capacity was recovered giving an immediate reversible capacity of 16.2 Ah. During the next 85 cycles the capacity of this now isothermal battery fell slowly to 14 Ah. The end of discharge *OCV*'s of the individual cells before and after the temperature excursion of cell 17 showed no permanent drift in the relative state of charge of individual cells.

The above experiment was repeated in full using a cell (cell 14) from the other series chain. It can be seen from Fig. 9 that a similar result was obtained, although the fall in battery capacity was even more marked.

Lowering the temperature of a single cell increases both its internal ohmic resistance and also its polarizability due to slower ion diffusion. Thus when the cell is cycling between fixed operating voltage limits, it can only operate over a much smaller region of its full reversible capacity. When the cell is connected into a battery, this effect is magnified by the limitations this cell imposes on the other cells in series with it. It is interesting to note that, despite this, little permanent loss in battery capacity had occurred when the battery was returned to the isothermal state. The temperature excursion studied was rather severe; in a practical battery one would expect a lesser temperature difference between single cells; more likely, variable temperature differentials covering large numbers of cells will be observed. This in itself should not badly distort the performance of the battery in the isothermal condition. One additional experiment, in which the temperature of one of the cells was raised to 400 °C for a few cycles, showed no significant change in the battery's capacity; obviously it was governed by the other 5 cells in this case.

Discussion

A battery of inter-linked Na/S cells has been experimentally operated for a period of 1.5 years and a total battery cycle life of 1325 cycles. Although limited cell substitution took place, 2 cells operated throughout this time, 2 others were still operating after 1280 cycles and one cell had achieved 905 cycles. Such undefeated long lives achieved under battery operating conditions are indicative of the quality of β-Al_2O_3 electrolyte tubes supplied by Chloride Silent Power Ltd.

No difficulties were experienced in operating the battery when all cells were functioning correctly.

The presence of at least one faulty cell caused a marked reduction in available capacity; however, its actual extent depended on the imposed operating conditions. One encouraging result was the remarkable stability of the reduced capacity on subsequent cycles; one might have expected a rapid continued decrease in capacity due to cells getting out of step.

Whilst it is true that many facets of operation of a multi-cell battery can be computed from single cell performance and elementary laws of electrochemistry, a parallel practical experiment is valuable in order to identify any unforeseen problems and also to provide an actual example to verify a theoretical treatment.

The factors governing the choice of cell interconnection patterns has been referred to at appropriate places. The actual choice for a particular application will have to be made for each battery, and also will include an estimate of the most likely cell malfunctions to be experienced. In brief one has the following factors to assess the desired array.

(1) Short series chains.

Disadvantage: High circulating currents in event of short circuit cell failure.

Advantage: Minimum parasitic cells in event of O.C. cell failure; No subsequent cycling of depleted chains in event of cell short circuit failure.

(2) Long series chains.

Disadvantage: O.C. cell failure or low capacity cell causes large parasitic loss.

Advantage: Low circulating currents in event of short circuit cell failure.

Superimposed on these basic options, other related factors influencing choice are the internal resistance of the individual cells and the operating conditions under which the battery is functioning.

Acknowledgements

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Reference

1 R. W. Minck, 7th Intersociety Energy Conversion Eng. Conf., San Diego, Sept. 1972.