SOME FACTORS AFFECTING SULPHUR ELECTRODE OPERATION IN SODIUM/SULPHUR CELLS*

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Summary

When sodium–sulphur cells are subjected to repeated charge/discharge cycles at a relatively high constant current density (100 mA/cm²) a considerable variation in charge acceptance can be obtained. This contrasts sharply with the cycling behaviour at constant voltage. The reasons for this are not yet clear, but several factors have emerged which profoundly affect sulphur electrode performance.

Four types of cycling behaviour have been identified: (1) near theoretical behaviour when the cell resistance changes very little with cycling; (2) the cell resistance increases with cycling over the whole range of charge and discharge without appreciable loss of capacity; (3) the cell resistance increases with cycling only in the two phase region during recharge, accompanied by loss of charge acceptance; (4) a large increase in resistance at the start of the discharge cycle accompanied by various recharge behaviours. Experiments using flat plate cells which demonstrate the differing characteristics will be described, and some of the reasons for these differences will be discussed.

Introduction

The construction of large sodium–sulphur batteries demands cells with reproducible and stable charge acceptance and resistance characteristics. Many cells show a slow decline in the former with cycling, and stable internal resistances are not easy to achieve.

Sodium–sulphur cells in the fully charged state consist essentially of reservoirs of sodium and sulphur separated by a membrane of sodium ion conducting beta alumina. Because of the low conductivity of sulphur, it is contained within an electronically conducting matrix (usually of carbon felt) which is in good contact with both the beta alumina and a pole or current

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collector which forms the cathode of the cell. In the discharge reaction, sodium ions pass through the beta alumina to form sodium polysulphides in the sulphur compartment. The discharge is normally terminated when a composition of Na_2S_3 is reached, and the cell is then termed 100% discharged. This operating range is governed by the phase diagram [1] and the operating temperature of 350 °C.

Recent performances of tubular cells, which can be optimized by suitable choice of charging regime involving a constant voltage charging mode, have been described by Piercy and Sudworth [2]. However, at high constant current densities, differences in behaviour between nominally identically prepared cells, and degradation of cell performance with time are accentuated. In earlier work at high constant currents inexplicable results were obtained when attempts were made to evaluate the comparative suitability of different grades of sulphur for use in the sulphur electrode.

Calculations by Gibson [3] based on his original steady state model [4], have shown that either a purely electronic or purely ionic resistance inserted between the pole and the matrix/melt does not appreciably alter the overall cell resistance. However, the distribution of current density between the pole and matrix is altered and this can have a profound effect on the cell performance.

If suitable values of resistance having both electronic and ionic components are associated with the pole surface then a high overall cell resistance can be predicted.

The present work was undertaken therefore to see if results similar to the irreproducible ones previously obtained could also be obtained by the deliberate experimental introduction of variations in the pole–matrix contact resistance, and if so to attempt to explain them in terms of pure ionic, pure electronic or mixed resistance based on Gibson's theory.

Experimental

Flat plate type cells have been used for these experiments, and a diagram of their construction is shown in Fig. 1. Their advantage over tubular cells is that they operate with a practically unipotential pole, and can easily be dismantled for post-mortem examination.

The cells were clamped into a suitable jig and operated with the beta alumina disc vertical in a fluidized sand bath at 350 ° C ± 5 °C. Constant current was applied using a potentiostat in the galvanostatic mode, and the cells were subjected to successive charge–discharge cycles by means of a system of relays. Termination of the cycles was by comparison of the cell voltage with preset voltage levels. The cell voltage was measured between the thin stainless steel discs on either side of the cell (AA in Fig. 1) between the heavier steel discs which carried the current leads.

The cells were filled with 500% Faradaic excess of sodium under nitrogen in a glove box. Sulphur electrodes were prepared by immersing the car-
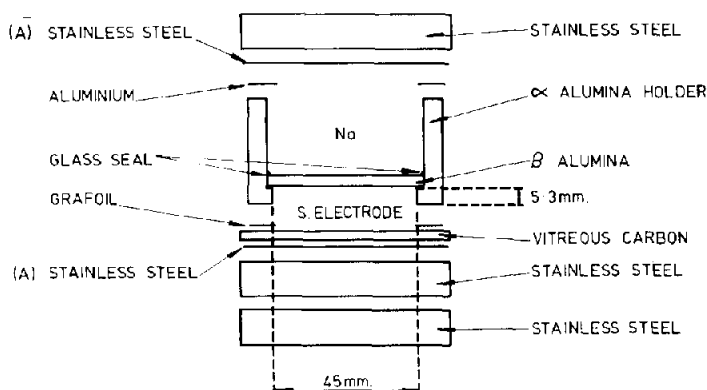
Fig. 1. Schematic diagram of flat plate sodium–sulphur cell.

bon felt in molten sulphur followed by hot pressing to the required thickness in a mould. Vitreous carbon poles (Le Carbone) were ground flat on both surfaces using an aqueous slurry of 600 mesh silicon carbide.

Cells were prepared and run subject to the following conditions, unless otherwise stated, and are then referred to as "standard cells": (a) Koch–Light 99.99% sulphur was used as received; (b) RVC 4000 carbon felt was used which together with the alumina assembly, pole and Grafoil sulphur gasket was desorbed overnight at 350 °C under vacuum before use; (c) charge–discharge cycles were carried out at 100 mA/cm^2. The area of beta alumina in contact with the sulphur electrode was 12.5 cm^2.

In addition to tests on the standard cells, tests were also carried out on cells to which the following variations in the pole–matrix contact had been made: (1) change of the sulphur electrode after the cell had been in use; (2) insertion of an electronic insulator between part of the pole and the matrix; (3) variation of pole–matrix contact by using metal poles; (4) variation of pole–matrix contact by placing a Grafoil insert between the pole and the matrix; (5) eliminating the pole–matrix contact by using an integral, one piece, pole/matrix; (6) introduction of a high resistance pole-felt contact, by using a high resistance felt.

Results

Standard cells

The performance of two nominally identical standard cells is shown in Figs. 2 - 5. Figures 2 and 4 show curves of cell voltage on charge and discharge *versus* electrode composition at various numbered cycles. The theoretical open circuit voltage is shown by the broken line and shows two regions. The horizontal plateau or "two phase" region represents the transition from pure sulphur to the composition Na$_2$S$_5$, during which the sulphur exists as a separate phase. The other, sloping, portion represents a change in composi-
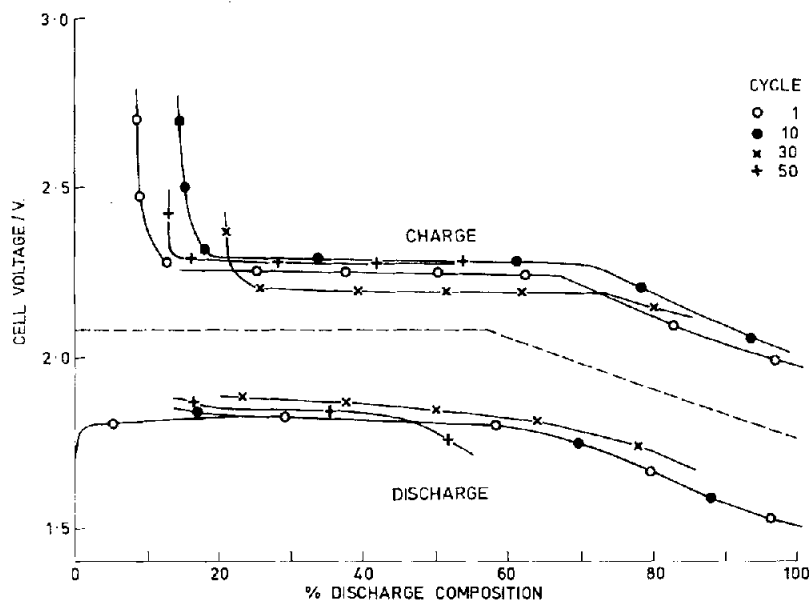
Fig. 2. Cell I. Voltage—composition curves. Points shown on these curves and curves in Figs. 4, 6 - 14 are *not* experimental points. They are merely marks to distinguish the curves.
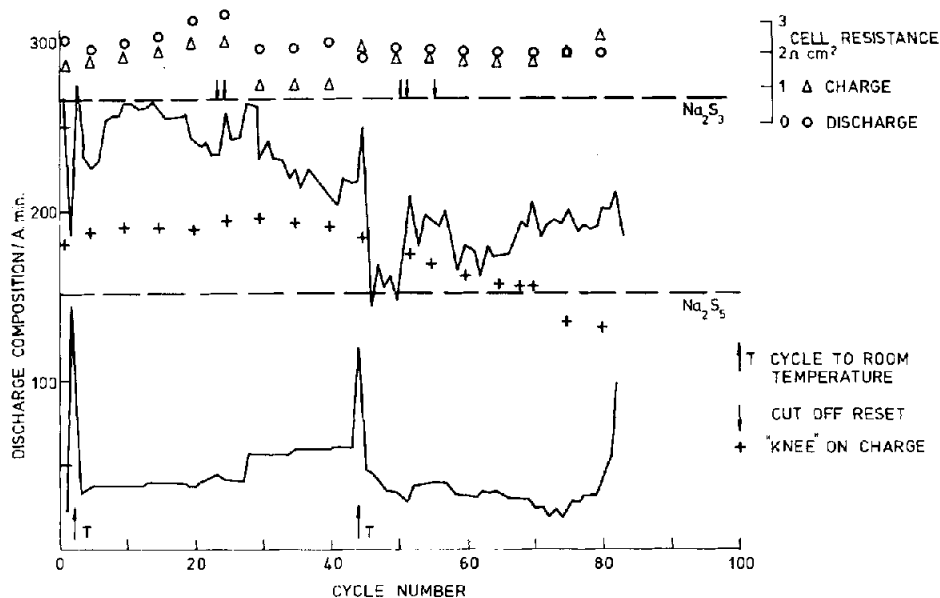

Fig. 3. Performance of cell I, coulometry.

tion from Na_2S_5 to Na_2S_3 and constitutes the "single phase region". The working curves of a normal cell (for example cell II, Fig. 6) approximately follow the shape of the open circuit curve except where recharge is terminated by polarization.
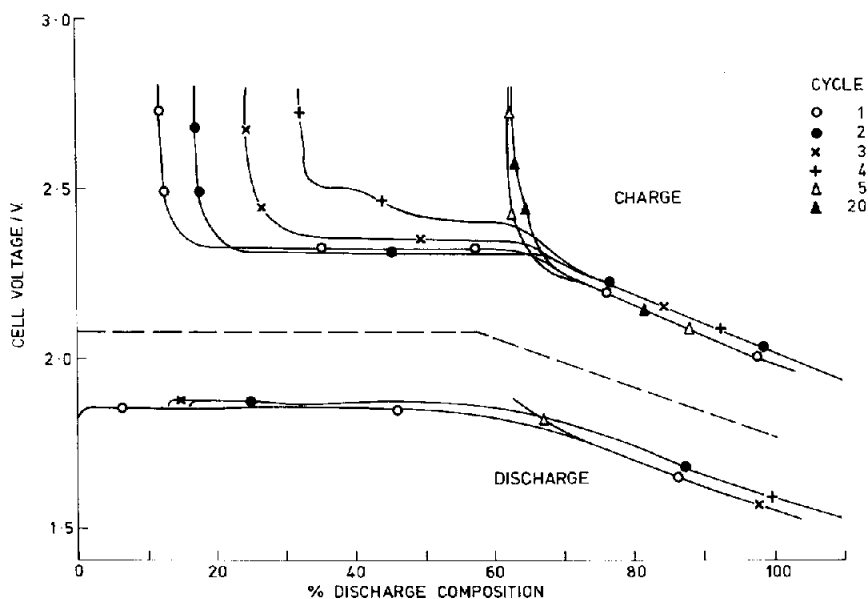
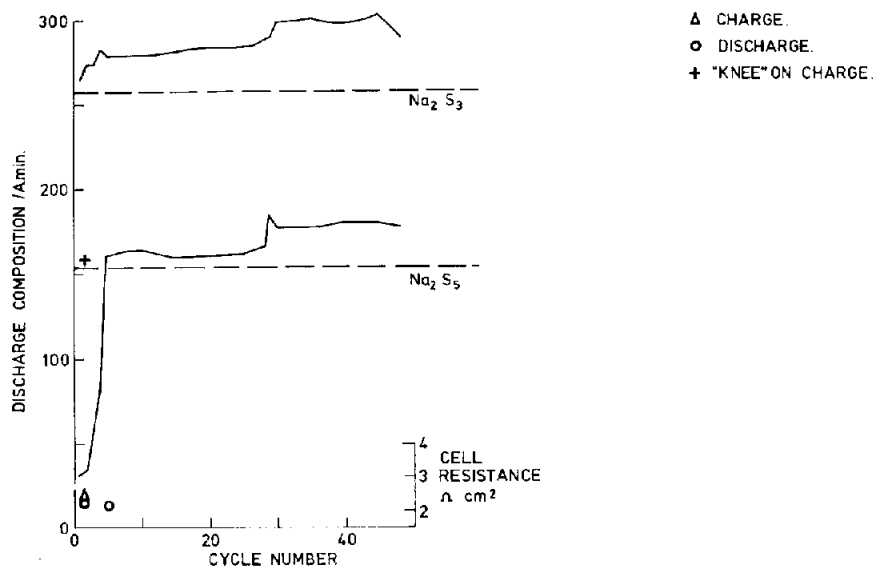Fig. 4. Cell II. Voltage–composition curves. First sulphur electrode.

Fig. 5. Performance of cell II, coulometry.

Cell resistances are calculated on charge using the overvoltage approximately mid-way along the two phase plateau, and on discharge from the "undervoltage" at the start of discharge.

The usual plot of cell coulometry against cycle number is shown in Figs. 3 and 5, in addition to the cell resistance. The latter is not shown where
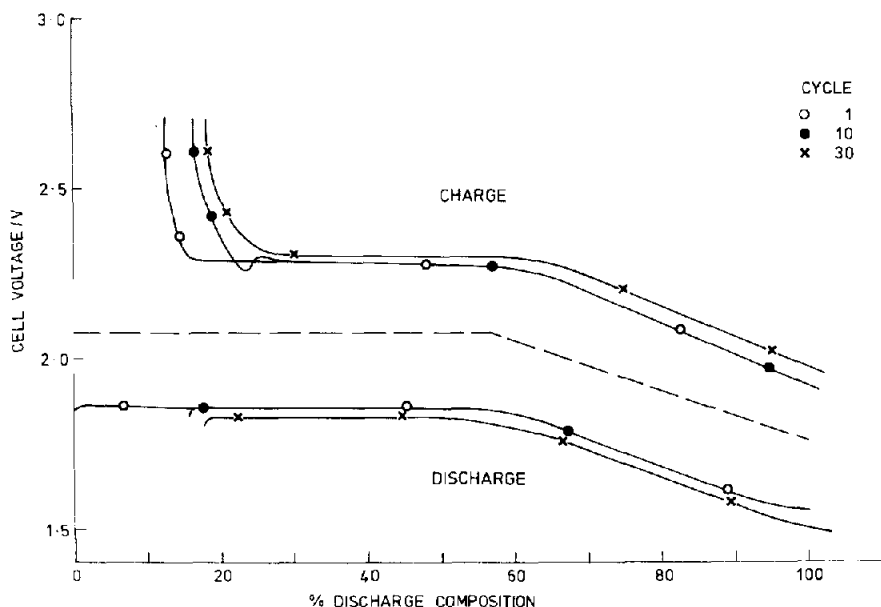
Fig. 6. Cell II. Voltage–composition curves. Second sulphur electrode.

the plateau region was not well defined. It is clear that the distinctive behaviour of cells is not evident from these plots, so they are not shown for subsequent cells.

The temperature cycles undergone by cell I, marked on Fig. 3, were accidental, due for example to failure of the compressed air supply to the sand bath. The erratic length of discharge was due in part to the sensitivity of the cut-off voltage to the general change in cell resistance, but increasingly as the cell aged to concentration polarization on discharge as seen in Fig. 2.

The cell resistance was also somewhat erratic, rising steadily at first, then decreasing abruptly around cycle 25, the "discharge resistance" having about twice the value of the "charge resistance" at this point. The cooling and reheating of the cell at cycle 44 increased the charge resistance again and removed the difference. The reasons for this behaviour are not known. The two phase region appears to be reached too early in the recharge cycle for most of the life of the cell; an effect which is often observed in this type of cell.

A contrast in behaviour is shown by cell II which after five cycles would not charge into the two phase region (Figs. 4 and 5). Inspection of the charge–discharge curves shows that the measured cell resistance increased in the two phase region on charge, but elsewhere remained almost constant.

Changing the sulphur electrode

Cell II was cooled and then carefully opened in a dry box. The sulphur electrode was removed and replaced by a freshly prepared standard electrode.

Cycling this cell produced the near ideal characteristics shown in Fig. 6. After 30 cycles the cell was still operating at over 85% of its nominal capacity.

At this stage the cell was again cooled and opened, and a thin layer of alumina wool inserted between the vitreous carbon pole and the felt matrix. Five evenly spaced holes had been made in this insulating layer, such that approximately 5% of the pole-carbon matrix contact was still present. Figure 7 shows some charge–discharge curves obtained with this configuration. The electrode resistance was very high on the first cycle and probably represents the electrode operating only via the holes in the insulating layer.
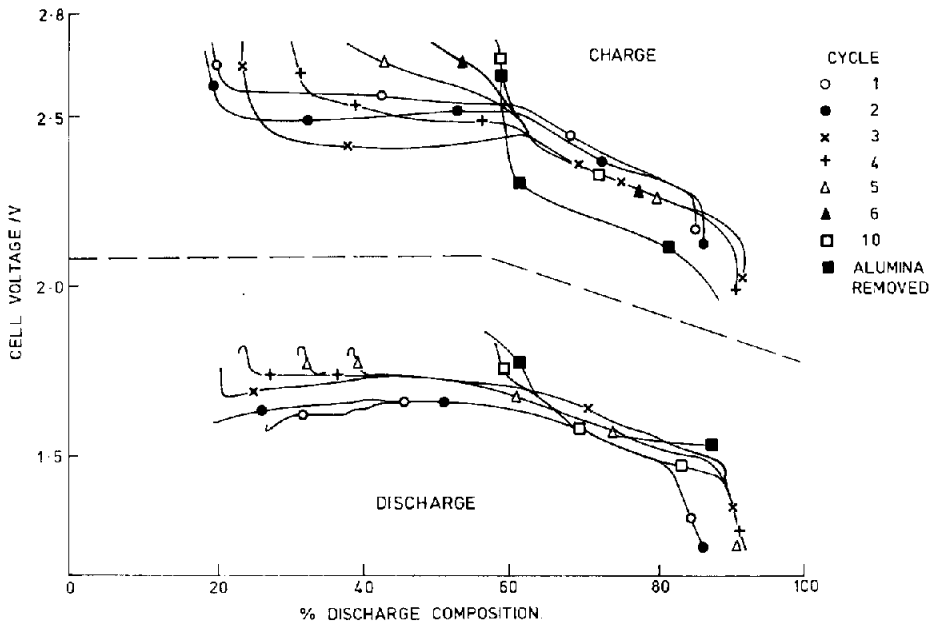

Fig. 7. Cell II. Voltage–composition curves. Alumina wool/pole.

It seems likely that the alumina layer would be preferentially wetted by sulphide, and the reduction in resistance in cycles 2 and 3 probably results from the sulphide filling this layer so that reaction can take place over all the pole surface. The rapid decreases in voltage observed at both ends of the discharge curve are probably also attributable to reaction at the pole itself. Further cycling showed progressively earlier polarization on charging into the two phase region.

After 10 cycles the final change in this cell was made. The composite electrode was removed, the alumina layer abraded off, and the electrode returned to the cell.

A subsequent charge curve shows that the cell resistance was much reduced, but the electrode would not charge into the two phase region.

The pole–matrix contact

A straightforward alteration to the pole–matrix contact is not easy to achieve, since most materials are readily corroded by sodium polysulphides at 350 °C, and most grades of carbon are porous to sulphur. However, two cells with metallic poles were constructed, so that electrode behaviour over at least the first few cycles could be studied.

Cell III was assembled in the standard manner but with a 347 stainless-steel pole, which was degreased by boiling in "Arklone". The voltage–composition characteristics are shown in Fig. 8. For the first 30 cycles this cell
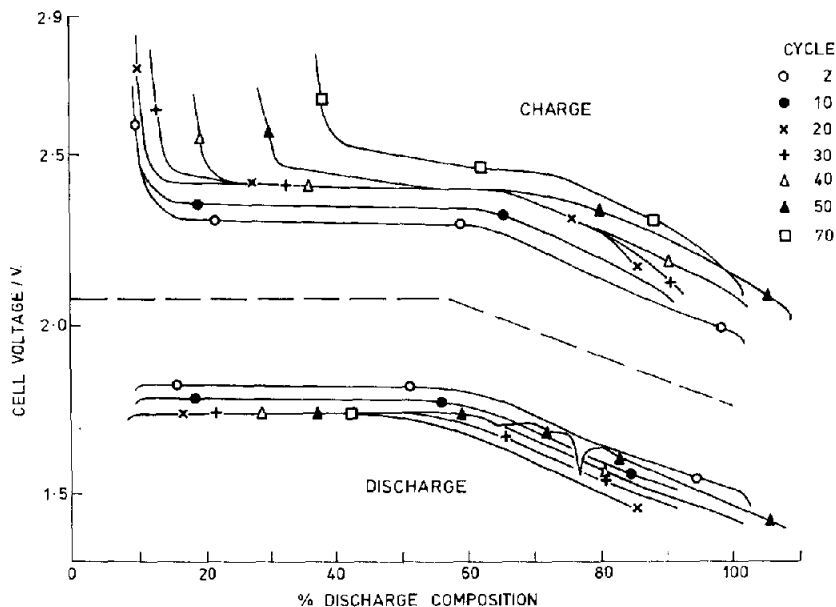
Fig. 8. Cell III. Voltage–composition curves. Stainless steel pole.

operated over at least 87% of its nominal capacity, and was still charging well into the two-phase region after 70 cycles. However, the cell resistance increased steadily up to cycle 20, and this increase was attributed to growth of a layer of corrosion products at the pole. After this the behaviour became more complex, and when the cell was cooled and examined after 89 cycles, black corrosion products were found on both the pole and beta alumina surfaces. However, it seems reasonable to attribute the increase in cell resistance during the early cycles to a deterioration of the pole felt contact.

A second cell (cell IV) with a metal pole utilized a sample of 1145 alloy aluminium foil with a 400 Å electron beam evaporated film of molybdenum* on the active face. Figure 9 shows the charge–discharge curves for this cell (IV), and the very rapid increase in cell resistance which occurred over
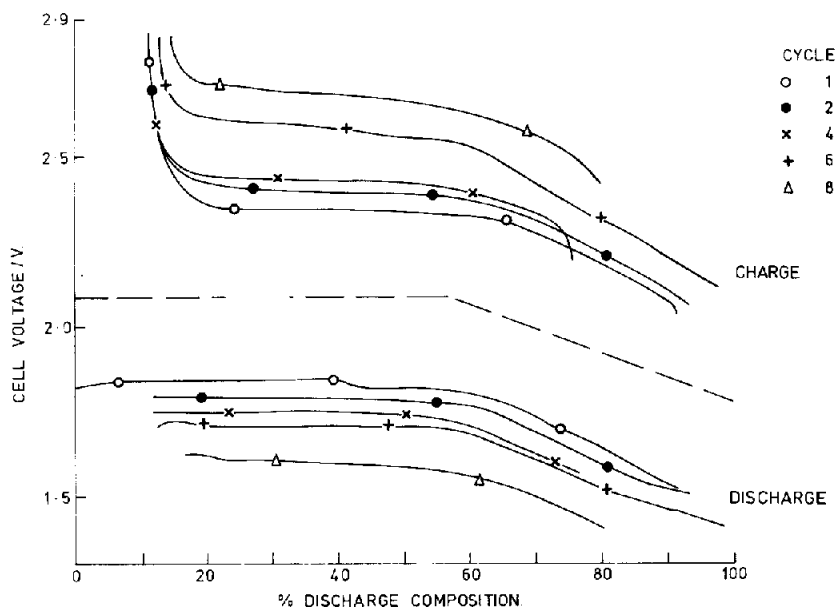
*Material supplied by Dow Chemical Co. (U.S.A.)

Fig. 9. Cell IV. Voltage–composition curves. Mo/Al pole.

only 8 cycles. The effect on the charge acceptance was not so pronounced. Examination of the cell after cooling showed that the molybdenum film had been entirely removed. The aluminium had presumably passivated giving rise to the increasing cell resistance. The reason for the higher resistance seen during recharge is not known.

Behaviour very similar to that of cells III and IV had been observed in a previous experiment with a standard cell made up with Berk "Molten" sulphur, which is a particularly pure commercial grade of sulphur. The characteristics of this cell (V) are shown in Fig. 10. In this case it is possible that a thin film of sulphur which was not reduced in subsequent discharge cycles was formed on the pole. It is notable that the cell charged to over 90% of its nominal capacity for at least 30 cycles.

Cell VI was assembled with a sheet of Grafoil inserted between the vitreous carbon and the sulphur electrode. The cell components were not desorbed prior to use in this case. The behaviour of this cell, shown in Fig. 11, resembled that of cells III and IV, with metal poles, in its early cycles but became more complex later. The "hump" at the start of the two phase region in cycle 5 and the subsequent higher than normal plateau voltage is not an unusual feature (see Figs. 4 and 7). Subsequent cycles showed a steady rise of voltage to cut-off, in contrast to the abrupt polarizations shown for cycles 1 and 5.

An obvious modification to the pole–matrix contact would be to construct the pole and matrix from one piece of material instead of relying on the normal pressure contact between the two. This can almost be achieved
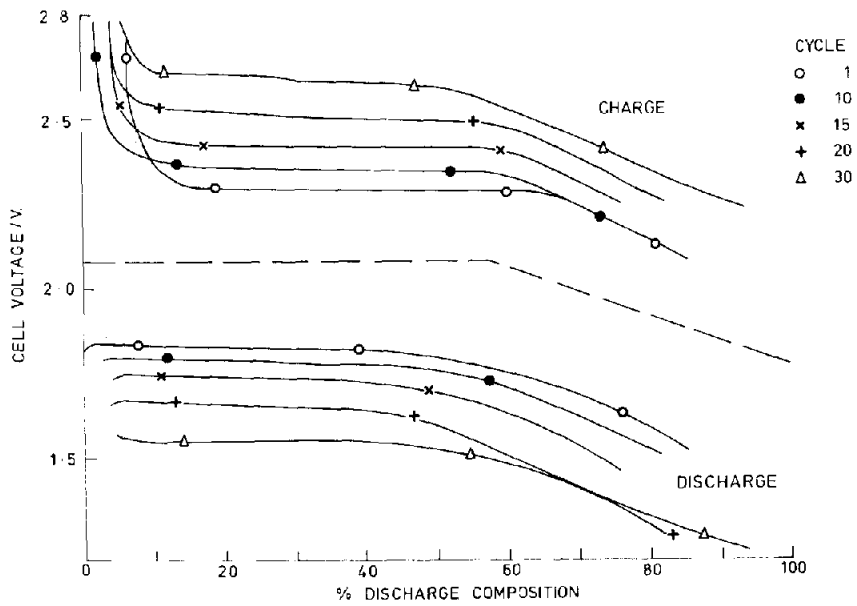
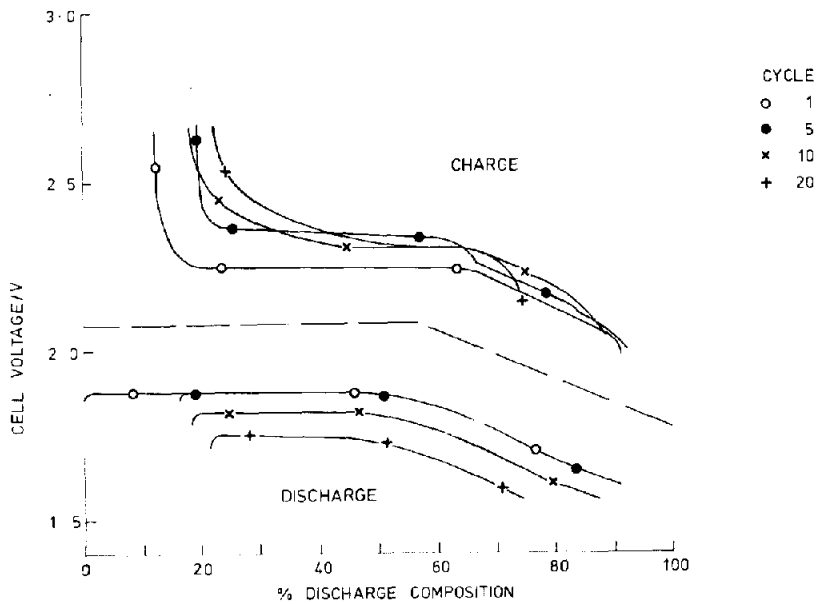Fig. 10. Cell V. Voltage–composition curves. Berk molten sulphur.

Fig. 11. Cell VI. Voltage–composition curves. Grafoil pole.

in practice by cementing carbon felt to a carbon pole using a bakeable car-
bon filled organic resin. Attempts to impregnate a flat plate electrode of this
type have so far failed, but a tubular electrode was successfully prepared and
cycled in a standard tube cell (cell VII). Charging curves at a constant cur-
rent of 60 mA/cm^2 are shown in Fig. 12. A detailed description of these
results is not appropriate in this paper, but it is notable that the resistance
in the two-phase plateau region varied very little, and that the polarization at
the end of charge was always sharply defined, in contrast for example, to the
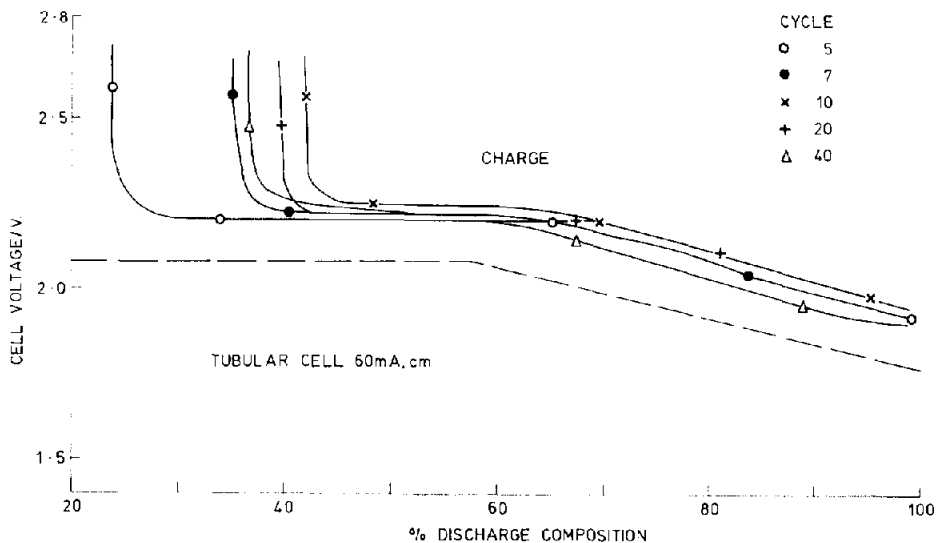behaviour of cell IV.

Fig. 12. Cell VII. Voltage–composition curves. Integral pole/matrix.

High resistance felt contact

Two cells were cycled in which a thin (5 mm uncompressed) layer of a
higher resistance carbon felt (Thornell VMA grade) was inserted between the
vitreous carbon pole and the normal sulphur electrode. For cell VIII, the
components were not vacuum desorbed, but the felts were heated in an oven
at 200 °C for about 4 h. The RVC 4000 was impregnated whilst hot. The
recharge characteristics of this cell were very good as shown in Fig. 13 and,
indeed, after cycle 29 the current density was increased to 125 mA/cm^2
without loss of capacity in the two-phase region. The exceptionally flat
characteristic in this region, with very little resistance change in 30 cycles,
is notable. However, the discharge characteristics are surprising and bear a
resemblance to those of cell II in Fig. 7 where alumina wool was present at
the pole.

It seems clear, that on recharge, the early formation of sulphur in the
vicinity of the pole was inhibited in this cell. However, some polarization
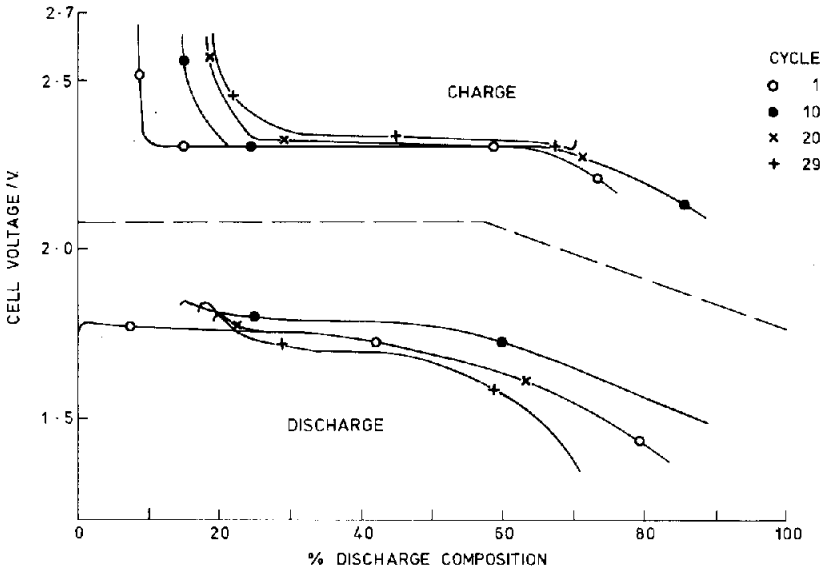occurred at the start of discharge, possibly due to the formation of lower

Fig. 13. Cell VIII. Voltage–composition curves. Heated VMA/pole.

sulphides on the pole itself, but clearly reasonable felt contact was main-
tained and the main body of the electrode was able to discharge but with
increasing concentration polarization.

Cell IX was identical to VIII except that the felts were not heated
prior to impregnation. As shown in Fig. 14, an entirely different behaviour
resulted. Discharge was normal, with very little variation in cell resistance,
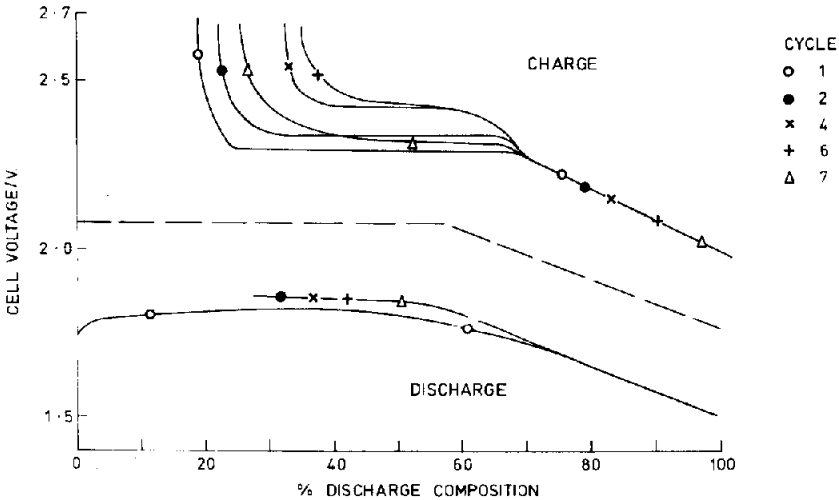but the recharge curves for the first six cycles show an increasingly raised

Fig. 14. Cell IX. Voltage–composition curves. VMA/pole.

plateau in the two-phase region. This increase is attributed to sulphur deposition in the vicinity of the pole. After cycle 6, the cell reverted to more normal behaviour, as shown by cycle 7 in Fig. 14. There was no apparent reason for this abrupt change of behaviour.

It seems possible that the heat treatment of the felts altered their wetting properties, either by some desorption process, or by oxidation of the carbon surface. It would be expected that a more polar surface would be preferentially wetted by sulphide.

Discussion

The operation of the sulphur electrode in a sodium–sulphur cell is complex. The behaviour of the basic extended electrode is not simple, as shown by Gibson's analysis [4], when contact resistances, inhomogeneity due to slow diffusion rates, differences in wetting characteristics and other similar changes during operation are not considered. The electrode reactions themselves are not simple, as shown by measurements performed on planar carbon electrodes [5, 6].

The results presented in this paper are for single cell tests, so no statement can be made about their reproducibility. The interpretation of these results must therefore be of a tentative nature until more results are available. It should be pointed out again that these cell characteristics were obtained using relatively high constant current densities, where effects due to uneven current distribution are enhanced and degradation of cell performance accelerated. However, examination of the results suggests that there are four basic patterns of behaviour.

The simplest behaviour is shown by cell II in Fig. 6, which is as close an approach to the theoretical behaviour as is normally obtained in practice, even at much lower current densities. Some initial small loss of capacity always occurs in practice, even with the best performances.

A second category of behaviour can be distinguished in which the cell resistance increases with each successive cycle over the entire range of both charge and discharge without appreciable loss of capacity. This is exemplified by cells III to VI inclusive, as shown in Figs. 8 to 11. In the case of the metal electrodes this can be attributed to the growth of a resistive corrosion film on the pole, although the situation is complicated in later cycles by the deposition of insoluble metal sulphides on the beta alumina surface. This deposition was particularly evident when cell III was examined after operation, but the cell had, by then, completed 89 cycles. The increased resistance in cell IV was thought to be due to separation of the Grafoil from the vitreous carbon by reactants. This was confirmed on post-mortem examination. The reason for this type of behaviour in cell V made with Berk Molten sulphur is unknown, and it can only be speculated that the resistance was due to deposition on the pole of some impurity present in the sulphur, which perhaps caused the sulphur to wet the pole and so form a film which interrupted the pole–felt contact.

According to Gibson's model, the increase in cell resistance in all these cases should be associated with a resistance at the pole surface having both electronic and ionic components. The distribution of reaction in the felt matrix is perhaps not much affected by these changes since there is no tendency towards early polarization on recharge. This absence of polarization also argues strongly against the increase in resistance arising at the beta alumina—felt interface, when polarization and rapid loss of recharge capacity would be expected.

The third type of behaviour which can be distinguished is that exemplified by cell IX (Fig. 14) and is also shown by cell II in Fig. 4. In this case the cell resistance rises to a high value in the two phase region on charge, and this value increases with cycling, but remains relative unchanged otherwise. At the same time, the charge acceptance in the two phase region is steadily reduced, and the cell shows increased polarization on each successive charge. Cell II eventually polarized at the start of the two-phase region. It is thought that this high resistance on charge is due to deposition of sulphur at and in the vicinity of the pole which wets both pole and felt surfaces, increasing both carbon–carbon and carbon–melt resistances. In this case, the current density in the felt is increased, resulting in the reaction becoming completely blocked at the electrolyte interface by sulphur deposition. If the felt matrix is cemented to the pole, as in cell VII (Fig. 12) then it is not possible for the pole–felt resistance to increase and, as expected, the high resistance in the two phase region is not seen. The charge acceptance does vary, and this may be due to deposition of sulphur in the vicinity of the pole on recharge, varying the current density in the felt so that earlier polarization takes place. However, this was a tubular cell, and is perhaps not strictly comparable with the others described, as inhomogeneities along the length of the sulphur electrode can tend to "smooth out" variations in the voltage characteristics.

Two cells are grouped in the fourth and last category on the basis of their discharge characteristics. The discharge behaviour of cell II (Fig. 7) with alumina wool, and cell VIII with heated VMA was similar in that both showed a rapid increase in resistance at the start of discharge. This is thought in the former case to be a polarization effect associated with the sulphide layer which remained at the pole after charging. The polarization in this cell is much more severe than the other, and probably results from the high current density at the holes in the alumina layer where the pole and felt matrix were in electronic contact.

The recharge curves of these cells bear little resemblance. The performance of the VMA cell (VIII) was excellent. It would seem that the VMA layer maintained good electronic contact with the pole, and that wetting of the fibres in the vicinity of the pole by sulphur was inhibited. In contrast, the alumina wool would act as an electronic insulator, so current could only pass to the felt via the direct contacts through the holes in this layer. Assuming the pole to be otherwise inactive the current density in these regions would be around 2 A/cm^2, and probably early deposition of sulphur at these holes was responsible for the subsequent polarization behaviour of the cell in the manner described in the third category.

Conclusions

The behaviour of the sulphur electrode can vary widely when operated at high constant current densities, depending on the detailed properties of the materials used in its construction. Despite this, patterns of behaviour can be identified which can easily be overlooked when the results are recorded only in terms of the coulometry. It appears that much of the variation in electrode performance observed in these experiments can be attributed to differences in the nature of the pole–matrix contact.

Acknowledgements

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