

IN-TEST AND POST-TEST ANALYSES OF SODIUM-SULFUR CELLS

MOTOI WADA, HIROYUKI KAWAMOTO and HISAMITSU HATOH

Advanced Reactor Dept., Hitachi Works, Hitachi Ltd., 3-1-1 Saiwai-cho, Hitachi-Shi, Ibaraki-ken 317 (Japan)

Summary

The electric potential profile on the sulfur electrode container, and the cell voltage fluctuation have been monitored by in-test analysis methods. The former provided information on where electrolyte cracking occurred, while the latter indicated when electrolyte cracking was likely to occur. As a post-test analysis method, X-ray CT photographs were taken of several of the tested cells. It gave information on the density distribution in the sulfur electrode, and the shape of broken electrolyte tubes.

1. Introduction

Cell lives of sodium-sulfur cells are often determined by degradation of the solid electrolyte. Solid electrolyte degradation will result in an increase of electrolyte resistivity [1], a decrease in faradaic efficiency [2] or even an electrolyte rupture which will lead to a cell temperature rise due to interaction of the components. These electrolyte degradations in actual sodium-sulfur cells are believed to be caused by the passage of sodium ion current across the solid electrolyte. The degree of degradation has been reported to be a function of the amount of charge passed through the electrolyte [4], and the breakdown of the solid electrolyte was observed to occur above some threshold [5]. For this reason, concentration of sodium ion current density is to be avoided to prevent the solid electrolyte from premature degradation and rupture, and the electrode structure for a sodium-sulfur cell should be determined with enough care to homogenize the current density distribution on the electrolyte. It is also desirable to test the cell carefully for its ability to homogenize the current density distribution.

With this in mind, we measured the longitudinal current density distribution of a sodium-sulfur cell by attaching probing terminals to the electrode container, and showed that the current density distribution of a vertically supported cell was inhomogeneous due to the effect of gravity [6]. We consider that this arrangement can be used to locate the position at which electrolyte cracking first occurs. We also report that electrolyte

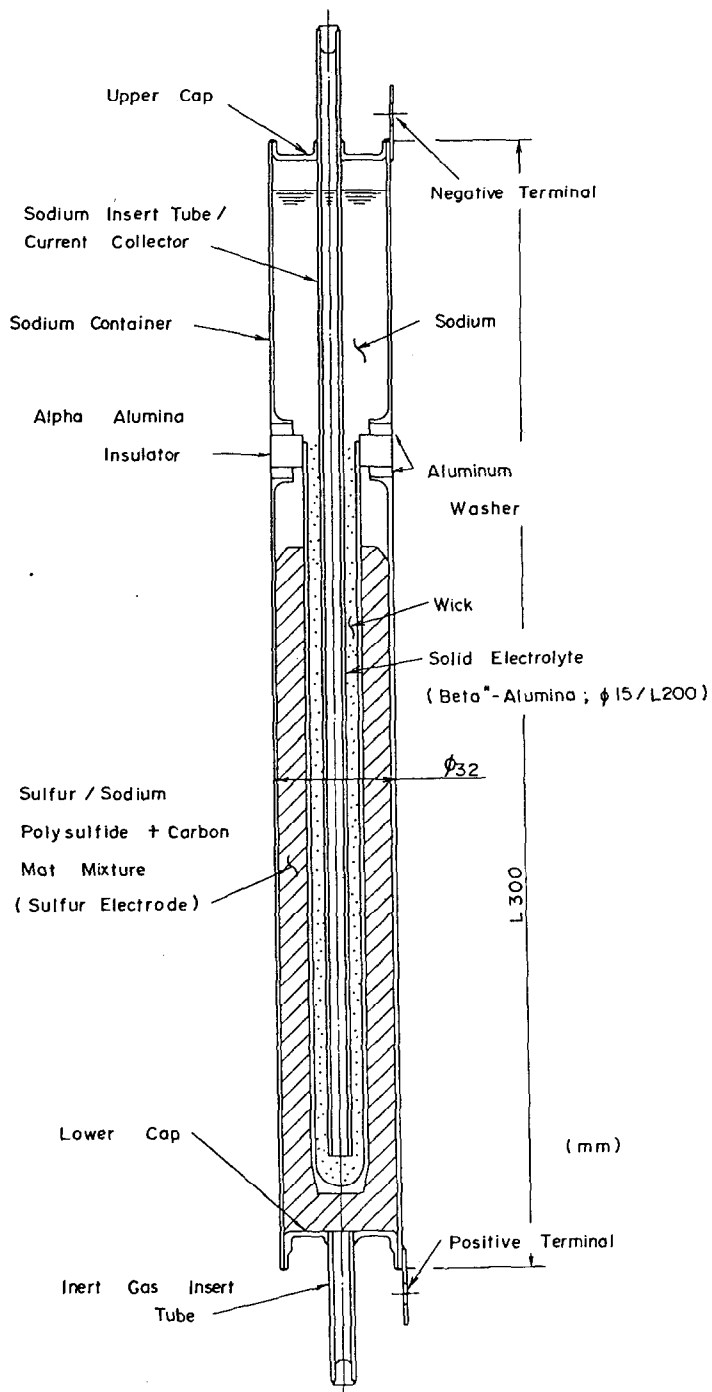


Fig. 1. Shape and dimensions of test cells.

cracking is accompanied by a cycling cell voltage fluctuation that appears several cycles before a noticeable electrolyte breakdown. Attempts were also made to measure the reactant density distribution in the sulfur electrode; an X-ray computed tomography system was found to be an effective tool for this measurement.

2. Test cell and setup

A cross sectional view of the test cell is shown in Fig. 1. The sulfur electrode was initially charged with pure sulfur embedded in graphite felt which had an electrical contact to the metal container. Sodium was injected under vacuum into the β'' -alumina solid electrolyte tube. Cell capacities were determined by the amount of sulfur and sodium contained in the cell, and were usually set to achieve 80 W h of discharge energy.

The arrangement is shown in Fig. 2. The cell charge and discharge were controlled by an automated cycler. Cell voltages and currents were recorded on a multi-channel, dot impact, strip chart recorder, and cell cycling data were obtained with a predetermined time interval and stored on a magnetic disk after analog to digital conversion. In addition to these charge-discharge cycle parameters, two to eight terminals were attached to measure potential differences between two points on the sulfur electrode metal container. Two thermocouples were attached to the cell wall to measure the temperatures of the sodium container and the sulfur electrode container. Cell voltage fluctuation was constantly monitored and recorded by a strip chart recorder. The magnetic oscillograph was used occasionally to measure the wave form of the voltage fluctuation, with a low pass filter to reject 50 Hz noise from the power supply.

Test cells were mounted on a stand in the furnace, which kept the cell temperature at about 330 °C during normal operating conditions. The recirculating air flow in the furnace could usually suppress the cell temperature rise within 100 °C on the occasion of solid electrolyte rupture.

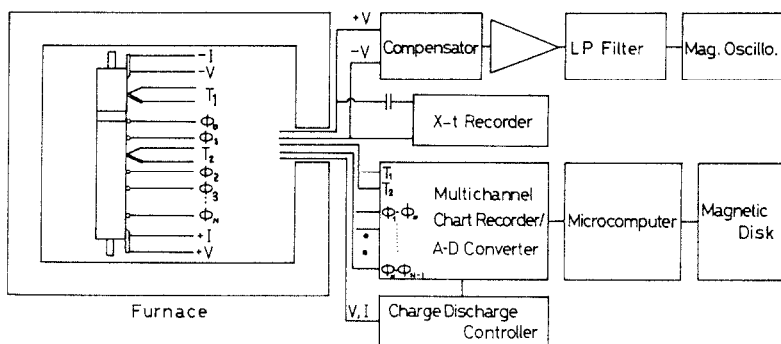


Fig. 2. Schematic diagram of the cell test setup.

3. Potential distribution on the sulfur electrode container at electrolyte cracking

By measuring the electrical potential distribution on the sulfur electrode container, one can estimate the longitudinal distribution of the electrode current flowing radially from the solid electrolyte to the metal container. When the solid electrolyte ruptures, the potential at the point where the reactants directly contact each other will decrease, and this electrical potential change will also appear on the potential signal of the metal container.

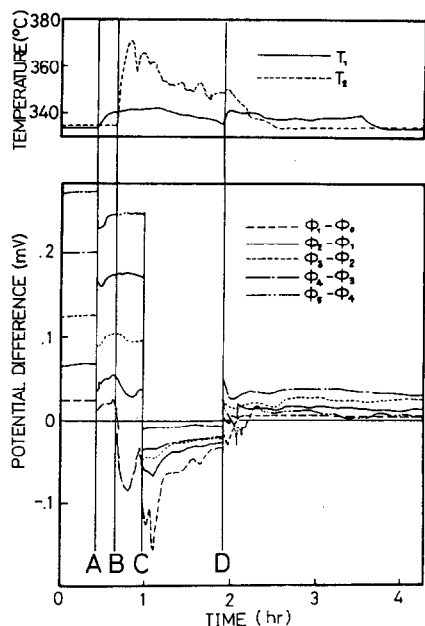


Fig. 3. Change of potential differences on the sulfur electrode container wall and their correlation with the measured cell temperatures.

Figure 3 shows an example of this kind of electrical potential change on the occasion of solid electrolyte cracking. For comparison purposes, temperature changes of sodium and sulfur electrode containers are also shown in Fig. 3. It will be seen from the Figure that at the time labeled A, potentials abruptly decreased and the temperature of the sodium container increased. This potential behavior corresponds to the decrease in electromotive force at the upper part of the sulfur electrode, and may be attributable to the direct reaction of sodium and sulfur due to cracking of the solid electrolyte. About fourteen minutes later, the temperature of the sulfur electrode container increased sharply and the potentials at the upper part of the container decreased sharply. (Point B in Fig. 3.) This behavior is considered to be caused by the precipitation of sodium in the electrolyte

tube to the sulfur electrode. At time C in Fig. 3, the discharge current applied to the cell was terminated. The potentials were then determined solely by the distribution of the reactants, and more negative potentials at the upper part of the electrode container indicated the lower electromotive force at this position. The reason for this smaller electromotive force may be due to a decrease in the sulfur molar fraction, and/or the formation of an electronic short circuit. Each of these effects can be caused by solid electrolyte cracking, and the potential profile in Fig. 3 shows that the initial crack appeared at the upper part of the solid electrolyte tube.

There was another jump in the electrode container potential profile at time D in Fig. 3. The Figure shows the potential distribution corresponding to the current flow from the top part to the bottom part of the electrode. This jump corresponds to either the initial crack at the upper end of the solid electrolyte tube, plugged by the lower polysulfides which should solidify at this temperature, or to another crack produced at the bottom end of the electrolyte.

4. Cell voltage fluctuation

The magnitude of the fluctuation in the cycling cell voltage was usually lower than 0.1 mV for a sound sodium-sulfur cell. However, a small ripple on the cell voltage was recognized as the cell test proceeded, and it became noticeable several cycles prior to apparent cell failure, which usually accompanied a cell temperature increase or a sudden drop in cell voltage. The trend of the appearance of this fluctuation is shown in Fig. 4. As shown, a very small ripple was recognized 9 cycles before apparent failure of the cell, and the fluctuation level gradually increased as the cell cycle advanced. The Figure also shows that the fluctuation is more noticeable during charge than during discharge. Resulting from a series of cell tests, it was found that the cell voltage fluctuation was usually more noticeable in the charge period, and apparent cell failure had occurred after one to several tens of cycles from the time that the noticeable fluctuation had been first observed.

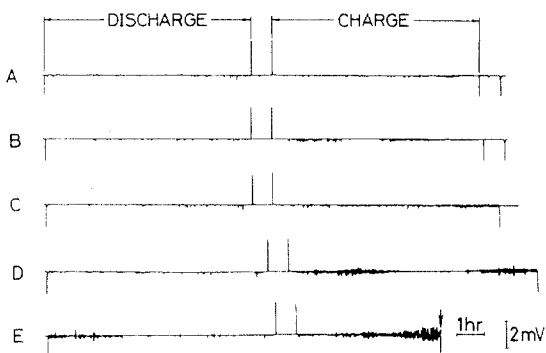


Fig. 4. Cell voltage fluctuation of a sodium-sulfur cell. A, 9 cycles; B, 5 cycles; C, 3 cycles; D, 1 cycle before apparent cell failure occurred at the arrowed position in E.

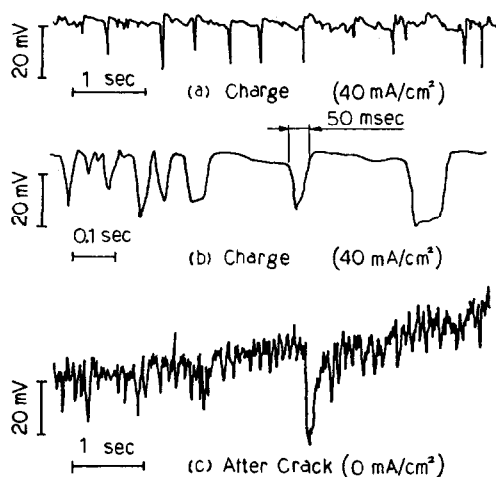


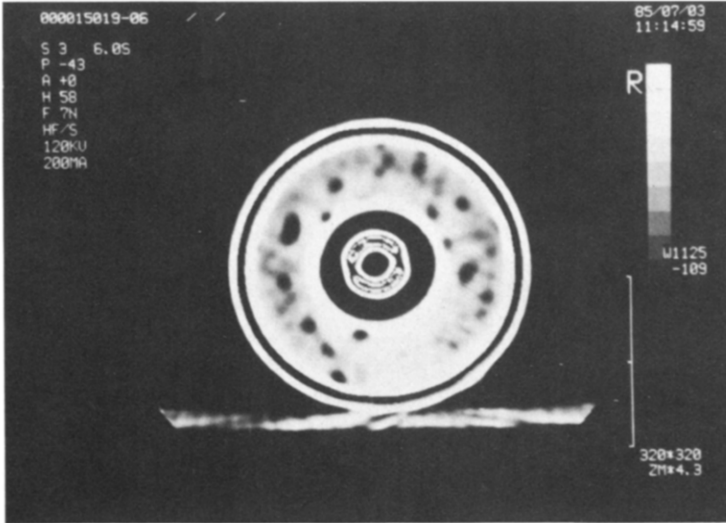
Fig. 5. Magnetic oscillograph trace of cell voltage fluctuation.

Figure 5 shows the wave form of the cell voltage fluctuation measured by the magnetic oscillograph. When the cell fluctuation first became noticeable, the wave form fluctuation was spiky, as shown in Fig. 5(a). Figure 5(b) shows that the time for a drop in cell voltage to return to the original level was, typically, of the order of 50 ms. After apparent cell failure, the cell voltage fluctuation became pronounced, and the cell voltage was never steady, even when the cell circuit was opened, as shown in Fig. 5(c).

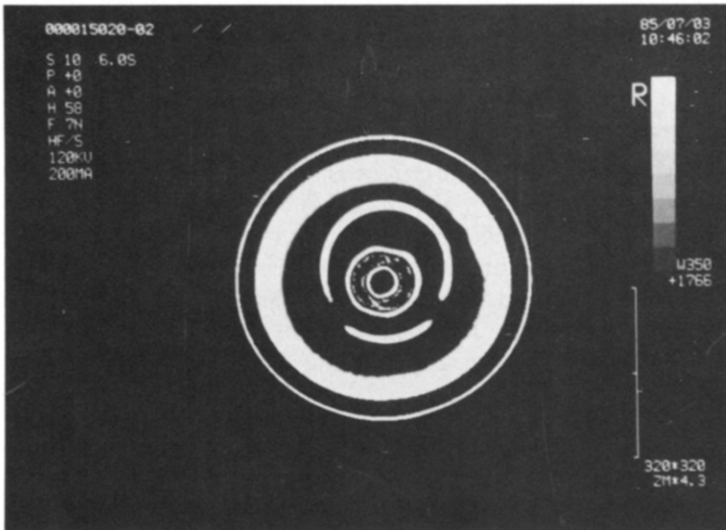
Though the reason for this cell voltage fluctuation is not known at present, it shows a strong correlation with solid electrolyte failure. In any case, it is useful to know when to stop a battery operation before the cells experience solid electrolyte rupture. Further study is necessary before this phenomenon can be applied to actual battery testing and operation.

5. X-ray CT test

The X-ray computed tomography systems used for medical purposes can be used to measure the density profiles of reactants in the sulfur electrode of a sodium-sulfur cell. Figure 6(a) shows the result of a density profile investigation of sodium polysulfides in the sulfur electrode using an X-ray CT apparatus (Hitachi Medical Corp. CT-W600). It is seen in the Figure that the spherically shaped areas, where the density is lower than in the other region, appear as circular shadows. These low density regions might be voids in the reactant. It is also obvious in the Figure that the reactant density is high both near the solid electrolyte surface and near the metal container. Testing of this sample cell was terminated after the discharge operation, and the photograph is consistent with the prediction from mathematical modeling of the sulfur electrode [7].



(a)



(b)

Fig. 6. X-ray CT photographs showing: (a) density profile at the centre portion of the sulfur electrode; (b) cross section of a broken solid electrolyte directly beneath the α -alumina insulator.

The X-ray CT photographs can often display the shape of a broken solid electrolyte tube after cell failure. Figure 6(b) is an example of such a case. From the photograph, one can see that the electrolyte tube was displaced laterally in the cell. X-ray CT photographs can provide this information without sectioning or dismantling a tested cell.

References

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