CHARACTERISTICS OF A LITHIUM–THIONYL CHLORIDE BATTERY AS A MEMORY BACK-UP POWER SOURCE

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Summary

An $Li/SOCl_2$ battery of R6 size (ER6C) has been evaluated as a memory back-up power source for CMOS RAM. The working voltage is 3.6 V and the discharge capacity is 1900 mA h on a 10K-ohm load. The cell exhibits satisfactory working voltage and discharge capacity over the temperature range −40 °C to 85 °C. The discharge reaction mechanism has been elucidated. Cumulative self discharge during 10 years discharge at 20 μA is estimated to be 3.5%. No serious problems have been observed during abuse tests.

Introduction

Recently, the demand for memory back-up power sources has increased dramatically. The requirements for such systems are high voltage, flat discharge curve, high energy density, wide operating temperature, excellent shelf life, and durability against abuse conditions. This paper describes the characteristics of the $Li/SOCl_2$ battery, which is considered to be the most suitable for memory back-up applications.
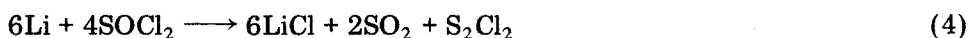
Cell construction

The cell design was of the bobbin type, since a current consumption for the CMOS RAM memory back-up is usually as low as 10 μA.

A lithium anode was pressed onto the inner surface of an outer can which was made of SUS304. The cathode bobbin (consisting of acetylene black with a Teflon binder) was located at the center of the can, and was isolated from the lithium anode by a glass separator. A solution of $SOCl_2$ with 1.2 M $LiAlCl_4$ served as the electrolyte, which also acts as a positive active material. A nickel current collector was designed to have a thickness of only 0.7 mm in order to avoid temperature rises or explosions that can be caused by an excess current flow when the cell is charged or short circuit. A glass-to-metal seal and a laser-welded hermetic-seal method were used.

The cell was 14.5 mm in diameter and 50.5 mm in height. The nominal capacity was 1900 mA h.

Discharge mechanism and performance

Many mechanisms have been advanced [1 - 4] for the discharge reaction of an $Li/SOCl_2$ cell, *e.g.*,

$$4Li + 2SOCl_2 \longrightarrow 4LiCl + S + SO_2 \tag{1}$$

$$8Li + 3SOCl_2 \longrightarrow 6LiCl + Li_2SO_3 + 2S \tag{2}$$

$$8Li + 4SOCl_2 \longrightarrow 6LiCl + Li_2S_2O_4 + S_2Cl_2 \tag{3}$$

$$6Li + 4SOCl_2 \longrightarrow 6LiCl + 2SO_2 + S_2Cl_2 \tag{4}$$

In order to clarify the discharge reaction mechanism, discharge reaction products were qualitatively analyzed by means of IR, GC and XRD. The reaction products detected were SO_2, LiCl and S, but Li_2SO_3 of eqn. (2), $Li_2S_2O_4$ of eqn. (3), and S_2Cl_2 of eqns. (3) and (4) were not observed. Qualitative analysis of SO_2 was carried out by means of GC, as shown in Fig. 1. The amount of SO_2 was found to increase as the discharge proceeded, and the rate of SO_2 formation was in good agreement with that expected from eqn. (1). Consequently, the main discharge reaction in the cell was thought to be represented by eqn. (1).

For low discharge rates, it is considered [5] that the cell discharge reaction takes place through an LiCl layer on the Li surface. On the other hand, when high discharge rates are used, the LiCl layer must be broken. Complex plane analysis (CPA) was carried out during discharge at various loads; the results are presented in Fig. 2. When the cell was discharged at more than 200 μA, the resistance decreased as discharge current increased, which
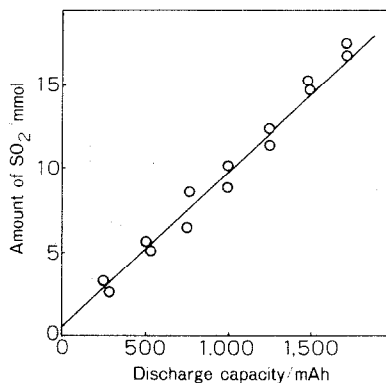

Fig. 1. Formation of SO_2 during discharge. Solid line gives the amount calculated from eqn. (1).
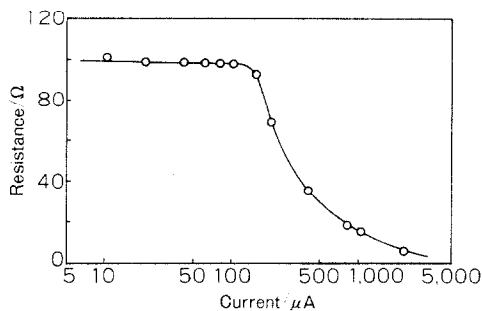
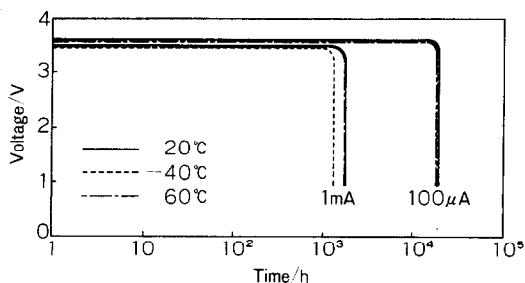Fig. 2. Relation between discharge current and resistance, as measured by CPA.

Fig. 3. Discharge curves of an ER6C cell at various temperatures and loads.

suggested that the LiCl layer was broken. However, when the cell was discharged at less than 100 μA, the resistance did not change, which indicated that the LiCl layer was stable.

Figure 3 shows the 1 mA and 100 μA discharge curves of an ER6C cell at various temperatures. The working voltages were as high as 3.5 V. The discharge curves were very flat over the temperature range -40 °C to 60 °C at both 1 mA and 100 μA discharge. When the cell was discharged at -40 °C under a 360 Ω load (corresponding to about 10 mA discharge), the working voltage reached 3.1 V and the discharge capacity was 900 mA h.

In some cases, the cells act not only as memory back-ups but also as power sources for pulse discharges of about 10 mA. One of the defects of the Li/SOCl$_2$ cell is a delay phenomenon when the cell is discharged at high drain. Figure 4(a) shows the voltage during the delay phenomenon *versus* the discharge resistance. With normal electrolytes, the temporary voltage drop is significant, as shown by "A" in Fig. 4(a). However, the voltage drop can be reduced to some extent, as shown by "B", when an electrolyte with an additive is employed. Figure 4(b) shows the pulse discharge characteristics of the ER6C cell which employs an electrolyte with an additive. The closed-circuit voltage during pulse discharge reached 3.2 V, even at -40 °C.
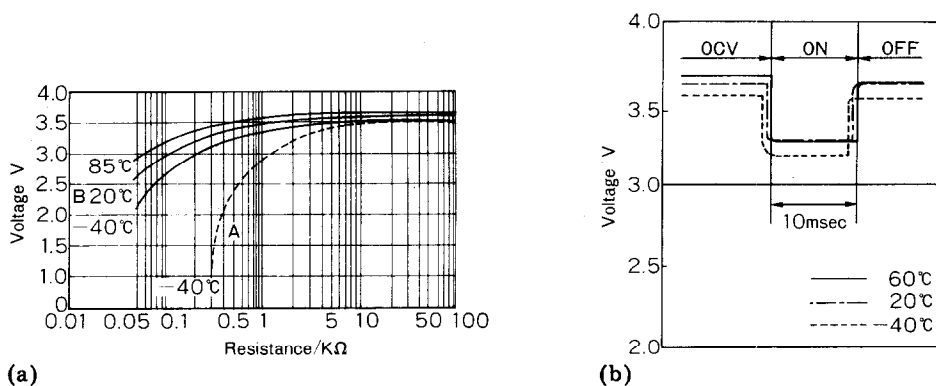

(a)

(b)

Fig. 4. Closed-circuit voltage characteristics of an ER6C cell. (a) Cell voltage during delay phenomenon *vs.* discharge resistance; (A) usual electrolyte; (B) with additive. (b) 10 mA/ 10 ms pulse discharge characteristics.

Self discharge

In CMOS RAM back-up use, shelf life is a very important parameter since the battery is expected to operate for nearly 10 years. An accelerated storage test at 60 °C for 200 days, which is considered to correspond to 10 years storage at ambient temperature, was carried out. The self discharge was only 55 mA h, or about 3% of the initial capacity.

An estimation of the self discharge during long periods of ambient temperature storage was achieved by means of a microcalorimeter. Figure 5 shows the change in heat generation rate during 20 °C storage; it can be seen that this rate decreases with time according to the given equation. This phenomenon can be explained by the fact that self discharge results in an increase in the thickness of the LiCl layer formed on the lithium anode and,
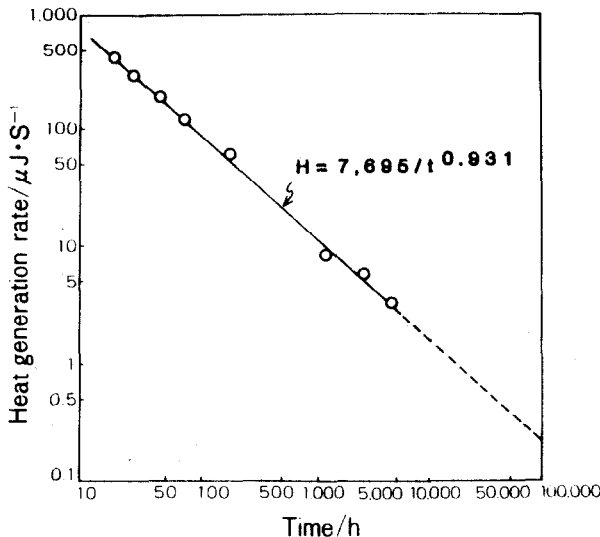
Fig. 5. Change in heat generation rate with storage time.

hence, a successive reduction in the self-discharge reaction in the cell. The cumulative self discharge can be calculated from the equation given in Fig. 5. The self discharge during 1 year was as large as 3.0% of the total capacity, but the cumulative self discharge during 5 years was only 3.3%, and that during 10 years was as small as 3.5%.

In order to clarify the influence of current on self discharge, the heat generation rates during discharge at various currents were measured. When the cell was discharged at relatively high currents, the self discharge was greater than that for the undischarging state. However, when the cell was discharged at currents as low as 20 μA, there was no change in the self discharge. These phenomena can be explained by the state of the LiCl layer during discharge, as described in Fig. 2.

Charge and abuse tests

When cells are used for CMOS RAM back-up, a voltage of 5 V is usually applied to the cell. The current flow to the cell will be less than 1 μA when the cells are protected by diodes and resistors. However, if the diodes and/or the resistors are faulty, a much larger current will flow to the cell. Consequently, it is very important that no capacity loss nor serious problems occur when the cells are charged in the circuit.

Figure 6 presents charge curves of an ER6C cell at 0.1 and 10 mA. In both cases, charge voltages were very stable except for a slight increase in the early stages. The voltage was kept below 4.1 V even at 10 mA charge. After charging at 10 mA for 150 h, the cell was discharged. No capacity loss was observed after the charge. This fact suggests that the active materials and other components in the cell were not changed by the charge. The charged
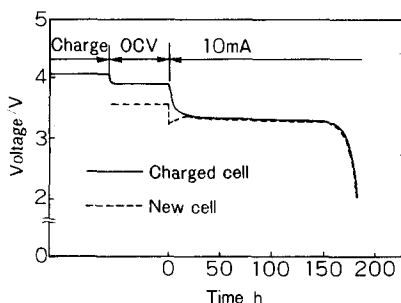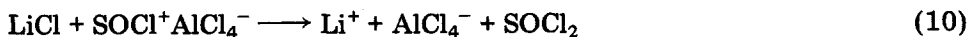

Fig. 6. 0.1 and 10 mA charge curves of an ER6C cell.

cell was analyzed. Although SO_2, Cl_2, S_2Cl_2, SO_2Cl_2 and SCl_2 were detected in the cell, the amounts of these species were very small. Accordingly, it is considered that almost all of the reaction products formed on charging must have reacted together to form the starting materials through the following transformations [6]:

$$SOCl_2 \longrightarrow SOCl^+ + 1/2\ Cl_2 + e^- \tag{5}$$

$$AlCl_4^- \longrightarrow AlCl_3 + 1/2\ Cl_2 + e^- \tag{6}$$

$$SOCl^+ + AlCl_4^- \longrightarrow SOCl^+AlCl_4^- \tag{7}$$

$$AlCl_3 + SOCl_2 \longrightarrow SOCl^+AlCl_4^- \tag{8}$$

$$1/2\ Cl_2 + Li^+ + e^- \longrightarrow LiCl \tag{9}$$

$$LiCl + SOCl^+AlCl_4^- \longrightarrow Li^+ + AlCl_4^- + SOCl_2 \tag{10}$$

Neither electrolyte leakage nor explosions were observed during and after the charge at 5 V, 10 mA and 130 mA.

The batteries were subjected to various abuse tests such as short circuit at 20 and 60 °C, forced discharge at 10 and 130 mA, storage at 85, 60 and −40 °C for 2 years, storage under vacuum at 85 °C for 150 h, and 10 thermal

shock cycles at 85 °C for 2 h and −40 °C for 2 h. In all these abuse tests, no serious problems were encountered.

Conclusions

It is concluded that Li/SOCl$_2$ batteries with the bobbin type of construction are suitable for memory back-up power sources because of their excellent performance.

References

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