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IMPROVEMENT IN DISCHARGE RATE AND LOW TEMPERATURE CHARACTERISTICS OF LITHIUM–IODINE CELLS

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Summary

An improvement in the discharge rate and low temperature characteristics of lithium–iodine cells has been made by the use of an additive, which is a charge transfer complex with lower resistivity over a wide temperature range, to poly-2-vinylpyridine iodide to form a cathode material. The improved cell can be discharged at several milliamperes (37 °C). The load voltage remains stable above 2.0 V under a constant current load of 10 - 20 μA even at temperatures as low as −50 °C. The donor weight of the additive is only about 0.7 - 1.4% of that of the cathode material.

Introduction

The lithium–iodine cell has been successfully used as a power source for cardiac pacemakers because of its advantages of high reliability, low self-discharge, and long lifetime [1]. However, its applications are still limited by its low discharge rate and poor low-temperature characteristics. The main reason for this is that the cell has a high internal resistance, which is mainly composed of three components, *i.e.*, the electrolyte–LiI layer resistance (R_e), the cathode resistance (R_c), and the interface contact resistance (R_i) between the electrodes (including anode and cathode) and the LiI–electrolyte layer. These three components of resistance are dependent upon the discharge process. R_e increases with the accumulation of the discharge product, LiI. R_c is a function of the iodine content in poly-2-vinylpyridine (P2VP) iodide; during discharge, iodine is depleted, gradually producing LiI, and R_c changes correspondingly. In the later stage of discharge, R_c increases rapidly. R_i is related to the resistivity, hardness, and viscosity of the contact materials, to the real contact areas, including surface roughness, and to the contact pressure. R_i also changes during discharge. In addition, the internal resistance is much influenced by temperature. The resistivity of LiI and P2VP iodide obey the Arrhenius formula and rise with decrease in temperature. R_i is also influenced by temperature, since the volume of solid components in the cell changes with temperature, in addition to the resistivity, hardness, and viscosity of the contact materials.

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Recently, some improvements in the discharge rate and low-temperature characteristics of the lithium–iodine cell have been obtained. The corrugated anode [2] and precoated anode techniques [3] of Mead *et al.*, as well as the pelletized cathode [4] of Schneider *et al.*, increased the discharge rate by several times. Sotomura *et al.* adopted a mixture consisting of 1-n-butylpyridinium polyiodide, or its derivates, and silica-gel powder as cathode materials [5], which can be discharged at several microamperes at 0 °C. Extensive work searching for high conductivity lithium ion materials has been carried out [6].

We obtained the reported results on improving the discharge rate and low temperature characteristics of the lithium–iodine cell by the use of an additive, which is a charge transfer complex with lower resistivity over a wide temperature range, to form a mixture with P2VP iodide as cathode material.

Experimental

(i) Preparation and characteristics of the cathode material

The cathode materials adopted in this experiment were mixtures involving P2VP iodide, the additive and iodine. P2VP iodide was prepared in an organic solution. Under certain conditions when solutions of P2VP and iodine were mixed together, a brown coloured precipitate of reaction product (*i.e.*, $P2VP{\cdot}I_2$) was obtained, the mole ratio of 2VP to I_2 could be as high as 1:1. The resistivity of $P2VP.I_2$ was relatively higher, about 10^7 ohm cm, and the compact density was relatively smaller, about 2 g/cm^3. However, when $P2VP{\cdot}I_2$ and nI_2 were mixed thoroughly, the resistivity of the mixture came close to a lowest value of 10^3 ohm cm, and its compact density became appreciably higher, ranging from 2.5 to 4.5 g/cm^3. The greater the iodine content of the mixture, the higher its density.

The additive, which is an iodine-containing charge transfer complex, was also prepared in an organic solution. The reaction product obtained was a black solid, which was fairly stable and did not melt at temperatures up to 200 °C. The resistivity of the additive material could be as low as 10 ohm cm. Furthermore, it changed only slightly over a wide range of composition. It is important that the resistivity of the additive material is obviously independent of temperature, because the additive material shows a very low apparent activation energy for electrical conductivity ($\leqslant$0.20 eV) which is better than that of $P2VP{\cdot}I_2$ (about 1.2 eV).

The additive, $P2VP{\cdot}I_2$ and I_2 were ground and screened separately and then thoroughly mixed. The cathode plate was formed by pressing in a steel mould. All the processes for making the cathode were carried out in a dry atmosphere.

(ii) Battery assembly and test

The experimental cell assembly was constructed in a steel mould by directly pressing the cathode plate together with the lithium anode sheet.

Lithium iodide electrolyte formed spontaneously when the anode was brought into contact with the cathode without adding any other electrolyte. The cell was mounted in a stainless steel case and then hermetically sealed by fusion welding. All the processes involved in the cell assembly took place under a dry atmosphere. The electrode reaction area was about 18 cm^2.

Cell tests comprised the determination of the voltage–ampere characteristics and discharge at different constant currents. Each current was maintained for one minute during the voltage–ampere test. The cells were maintained at the desired temperatures for over 6 h before testing.

The experimental test cells were divided into three groups according to the different cathode materials: the first, group A, was composed of $P2VP \cdot I_2 + nI_2$ without additive; the second, group B, consisted of additive + nI_2 without $P2VP \cdot I_2$; the third group C, of additive + $P2VP \cdot I_2 + nI_2$.

Results

Figure 1 shows typical *V–I* curves of A, B and C cells after discharge at 30 μA, 37 °C, continuously for one month. The curves of the A and B cells almost overlapped as shown. The characteristics of the C cells are obviously better than those of the A and B cells.

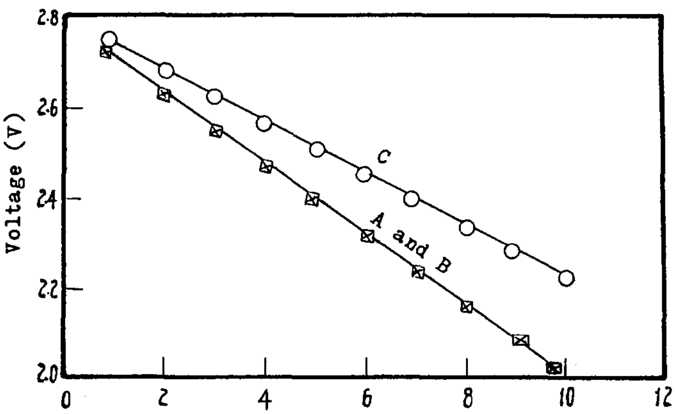

Fig. 1. Typical *V–I* characteristics at 37 °C. A, B, and C cells were tested after one month of continuous discharge at 30 μA and 37 °C. Each test current remained constant for one minute.

Figure 2 shows typical low temperature *V–I* curves of A, B and C cells after eight months of continuous discharge at 30 μA, 37 °C. Of the three types of cell, the low temperature *V–I* characteristics vary in the order C, B and A. Cell C is still superior to cells B and A even when tested at −50 °C. As mentioned above, the additive was added to cells B and C, but not to cell A. The additive evidently played an important role in the improvement of

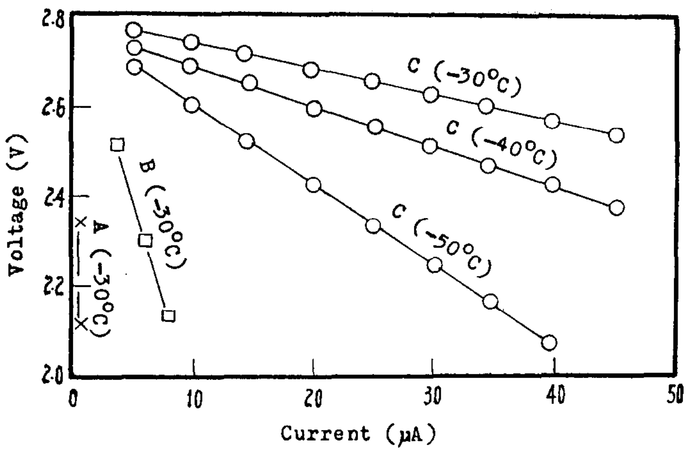

Fig. 2. Typical V–I characteristics at different low temperatures. A, B and C cells were tested after eight months of continuous discharge at 30 μA and 37 °C. Each test current remained constant for one minute.

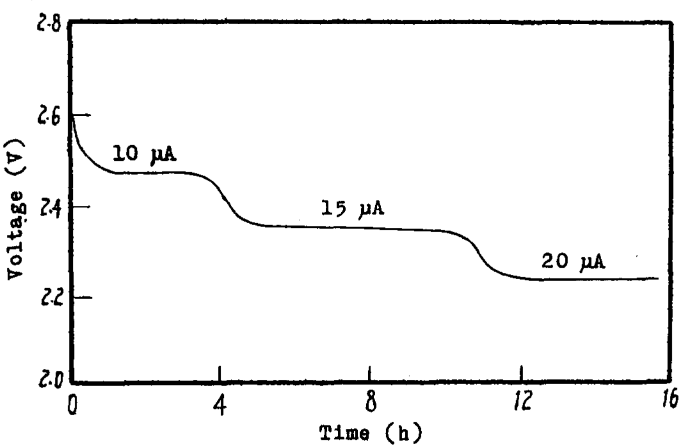

Fig. 3. Typical discharge characteristics of the C cell at −50 °C after eight months continuous discharge at 30 μA and 37 °C.

the low temperature V–I characteristics of the cells. The weight ratio of the additive to iodine in the composition of the B cell cathode material which led to the optimum low temperature V–I characteristics, was 1:15. The donor weight of the additive in the composition of the C cell cathode was only in the range 0.7 - 1.4% of the cathode weight, and the weight ratio of the two donors (including the additive donor and P2VP) to the acceptor (iodine) was in the range 1:9 - 1:37. In fact, a small amount of additive donor saved some of the P2VP.

Figure 3 shows the typical discharge curves of type C cells at constant currents of 10, 15 and 20 μA at −50 °C after eight months continuous discharge at 30 μA, 37 °C. The Figure demonstrates that the type C cell can still be discharged at low temperatures down to −50 °C with good performance, even after having discharged continuously for eight months, which corresponds to an average accumulation of 48 mg of LiI over an area of 1 cm^2 of reaction electrode. Therefore, it seems that the type C cell is capable of long term discharge at several microamperes at low temperatures.

Conclusion

In considering the discharge rate and low temperature characteristics, the experimental results show that the type C cell is the best, the type B cell comes second, and the type A cell is the wcrst. Therefore, we suggest that the type C cell composition can be used effectively to improve the discharge rate and low temperature characteristics of lithium–iodine cells. The function of the additive and the P2VP.I_2 on the performance of lithium–iodine cells is to be investigated.

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