Use of iodine-2,2'-azinobis (3-ethylbenzothiazole-6-sulphonate) mixture as cathode in a solid state cell

S AUSTIN SUTHANTHIRARAJ and P MARUTHAMUTHU

Department of Energy, University of Madras, A C College Campus, Madras 600 025, India

MS received 14 March 1989; revised 19 April 1989

Abstract. A new solid state test cell having a configuration of (–) Ag, $\text{Ag}_6\text{I}_4\text{WO}_4/\text{Ag}_6\text{I}_4\text{WO}_4/\text{I}_2$, ABTS (+) [ABTS: 2,2'-azinobis (3-ethylbenzothiazole-6-sulphonate)] has been investigated through polarization and ageing studies. The cell has an open circuit voltage and short circuit current of 640 mV and 18.5 μA respectively at room temperature.

Keywords. Solid state cell; 2,2'-azinobis (3-ethylbenzothiazole-6-sulphonate); solid electrolyte; cathode; polarization.

1. Introduction

The market potential for self-contained and portable batteries for day-to-day applications, for instance power tools, toys and cost-effective batteries in place of expensive Ni–Cd cells, is quite attractive. In spite of the fact that practical considerations for large-scale production are currently at an early stage and much more developmental work needs to be completed, recent efforts have indicated the possibility of developing new fabrication technologies for such batteries. The technical feasibility of such solid state systems, capable of operating flash lights has already been explored at Harwell (Hooper and Tofield 1984).

The primary requirement of a solid state cell is an electrolytic medium characterized by high ionic conductivity with negligible electronic mobility. The choice of cathode materials for solid state electrochemical cells is governed by two factors: (i) the cathode reversible potential should be less positive than the decomposition potential of the electrolyte, and (ii) the half-cell reaction must be electrically compatible with the mobile ion in the electrolytic phase. In order to reduce electrode polarization effects, particularly cathode polarization which generally results in loss of power output, it is necessary to use electronically conducting iodine charge transfer complexes as cathodes in silver iodine batteries (Vincent *et al* 1984). Power ratings of a silver anode primary battery system, constituted by five cells in the series mode, with $\text{Ag}_6\text{I}_4\text{WO}_4$ as the solid electrolyte and the I_2 –phenothiazine charge transfer complex as cathode have been reported in our earlier work (Suthanthiraraj 1986).

This paper deals with our investigations on a silver–iodine solid state cell having a new cathode mixture containing 2,2'-azinobis (3-ethylbenzothiazole-6-sulphonate) (ABTS) and iodine. From the family of stable silver ion conductors, $\text{Ag}_6\text{I}_4\text{WO}_4$ has been chosen as the electrolyte.

2. Experimental

2.1 Materials

2.1a ABTS: A Boehringer (West Germany) sample of 2,2'-azinobis (3-ethyl-

benzothiazole-6-sulphonate) in the form of a diammonium salt having a formula of $C_{18}H_{16}N_4O_6S_4-(NH_4)_2$ was used as such.

2.1b Anode: A mixture of 99.9% pure silver powder (40 mg) and $Ag_6I_4WO_4$ solid electrolyte powder (10 mg) was used as the anode. The incorporation of the electrolyte in the negative electrode structure is to maximise the anode/electrolyte interface area and to ensure the best interfacial contact between the electrode and electrolyte layers.

2.1c Cathode: The cathode was a complex containing iodine (30 mg) and ABTS (20 mg).

2.1d Electrolyte: $Ag_6I_4WO_4$ solid electrolyte was synthesized from AnalaR grade chemicals of AgI, $AgNO_3$ and $Na_2WO_4 \cdot 2H_2O$ as suggested by Takahashi *et al* (1973) and examined by powder X-ray diffraction and electrical conductivity techniques. 500 mg $Ag_6I_4WO_4$ was used as electrolyte in the cell.

2.2 Cell design

A circular cell of 8 mm dia and 4 mm thickness was fabricated by pressing the three cell components together at a pressure of 4 ton cm^{-2} . The button cell thus prepared was placed between two silver foils (the anode face was directly attached to the foil while the cathode face was held via a graphite disc, acting as a current collector). This stack was mounted between two ebonite discs through screw arrangements and electrode leads taken out for measurements.

2.3 Cell performance

The button cell was drained at different currents and the values of voltage corresponding to each load resistance measured using a Keithley 614 Electrometer. The cell was kept at 30°C for a period of 90 days and various polarization effects analysed through performance plots.

3. Results and discussion

3.1 Discharge features

Typical discharge curves for the cell operating at 30°C under various loads are shown in figure 1. These isothermal curves corresponding to constant loads 15, 47, 150 k Ω and open circuit conditions, respectively, are similar in shape, indicating a well-defined mechanism of the electrode processes. The open circuit voltage of the fresh cell has been found to be 640 mV against a theoretical value of 687 mV. In fact, the presently observed open circuit voltage value coincides with that obtained with an I_2 phenothiazine cathode. This is due to the fact that the overall cell reaction remains the same in all the cases based on the Ag^+ ion motion. It is also clear from figure 1 that low current discharges are more stable than the high current ones.

Figure 1. Discharge curve under various loads at 30°C. (a) Open circuit voltage, (b) load resistance 150 kΩ, (c) load resistance 47 kΩ, and (d) load resistance 15 kΩ.

3.2 Polarization behaviour

Performance curves for the cell as a function of the period of storage are represented in figure 2. The initial performance of the present cell is quite significant and it is much better as compared to that of earlier versions of $\text{Ag}_6\text{I}_4\text{WO}_4$ -based cells. From figure 2 it is clear that there is a fall in terminal voltage from its initial value as the drain current progresses. This almost linear region of low current drains can be attributed to the internal resistance of the cell components. Such voltage loss, known as the "iR polarization" has been observed in a variety of electrochemical cells (Suthanthiraraj 1986b). However, at very high current drains, the observed phenomenon of rapid fall in cell voltage may be considered as due to the presence of iR polarization coupled with another kind of polarization called "electrode polarization". Electrode polarization occurs as a result of the depletion of electroactive materials at the electrode surfaces. Also, it may be observed that a gradual increase in the internal resistance of the cell takes place on storage, owing to the formation of low conductivity reaction products viz. $\beta\text{-AgI}$ or $\gamma\text{-AgI}$.

Iodine and ABTS have been reported by Maruthamuthu *et al* (1987) to undergo a reversible reaction,

Figure 2. Performance plot of the cell as a function of storage period (a) Initial and (b) after 25 days of storage.

in which the radical cation ABTS^+ is very stable even in the absence of any other additives. The equilibrium constant, K , for the above reaction has been estimated to be 1.43×10^2 . Incorporation of the iodine-ABTS mixture as the cathode material would provide a continuous supply of I^- ions. During discharge, the silver ions travel from anode to cathode, and react with these I^- ions resulting in the formation of AgI at the electrolyte/cathode interface. If the cell discharge occurs continuously, AgI content at the cathode/electrolyte interface increases and hence a fall in cell voltage occurs.

3.3 Effect of ageing on power ratings

Using the experimentally observed values of cell voltage and discharge current at various loads, the power values have been evaluated and the results shown in figure 3. The occurrence of a finite value of maximum power (P_{max}) and its shift towards a lower point after storage is due to the fact that the power yielding capability of any cell is a characteristic feature of the system depending upon both the electrode potentials.

Figure 3. The power of the cell as a function of voltage. (a) Initial and (b) after 25 days of storage.

3.4 Rated capacity and cell resistance

Figure 4 compares the capacity and internal resistance of the cell as a function of storage interval. The observed exponential decrease of the capacity with time is closely associated with an exponential increase of internal resistance. In practice, all cells exhibit certain internal losses wherein one or both of the electroactive materials is consumed and there are internal ohmic losses as well.

4. Conclusions

The system $\text{Ag}, \text{Ag}_6\text{I}_4\text{WO}_4/\text{Ag}_6\text{I}_4\text{WO}_4/\text{ABTS} + \text{I}_2$ has been found to represent an all-solid-state microwatt power source suitable for ambient temperature applications. However, the internal resistance of the cell inhibits reasonably long shelf life.

Figure 4. Effect of ageing on capacity and internal resistance of the cell.

References

- Hooper A and Tofield B C 1984 *J. Power Sources* **11** 33
 Maruthamuthu P, Venkatasubramanian L and Dharmalingam P 1987 *Bull. Chem. Soc. Jpn.* **60** 1113
 Suthanthiraraj S A 1986a *Bull. Electrochem.* **2** 553
 Suthanthiraraj S A 1986b in *Materials for solid state batteries* (ed.) B V R Chowdari and S Radhakrishna (Singapore: World Sci. Publ. Co.) p. 423
 Takahashi T, Ikeda S and Yamamoto O 1973 *J. Electrochem. Soc.* **120** 647
 Vincent C A, Bonino F, Lazzari M and Scrosati B 1984 *Modern batteries* (London: Edward Arnold) pp 212