

EFFECT OF ADDITION AGENTS ON THE REDUCTION OF DIVALENT SILVER OXIDE

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ABSTRACT

This paper reports the results of investigation carried out on the preparation of silver (II) oxide by the chemical method and electrochemical reduction of silver (II) oxide with and without additional agents. The results indicate that a suitable composition of the material with additives can give single-stage discharge.

Key words: Silver oxide, discharge characteristics, reduction behaviour.

INTRODUCTION

The important problems in the silver oxide-Zn button cell are voltage stability, cell stability and shelf stability. In spite of a two-stage discharge voltage, divalent silver oxide received more attention because it gives larger energy density. The presence of first plateau renders divalent silver oxide unsuitable for several applications. Therefore several workers [1-3] have described the effect of mechanical mixing of silver [II] oxide and silver [I] oxide and current density on shortening the length of upper plateau. The effect of additives on the discharge of silver oxide-zinc button cells has been investigated [4-5]. This paper reports the electrochemical reduction behaviour of silver (II) oxide with additives viz. lead dioxide and manganese dioxide. This silver oxide cathode composition is found suitable to give voltage stability with high energy density in AgO-Zn button cells.

EXPERIMENTAL

Method of preparation of divalent silver oxide

The Ag_2O produced by precipitation of silver nitrate with potassium hydroxide is heated at $60^\circ C$ in the presence of potassium persulphate with continuous stirring to oxidise it to AgO . The precipitated silver (II) oxide is then dried below $50^\circ C$. This freshly prepared silver (II) oxide is used in all the experiments.

Fixed quantity of silver (II) oxide (0.3 g) powder is pressed in a hole of diameter 9.5 mm made on the square perspex sheet. Silver wire wound in the circular form fixed in the hole and the other end coming through the perspex sheet is used as the lead for contact. After standardisation of pressure, silver (II) oxide is pressed over silver wire with addition of

carboxymethyl cellulose binder. The pressed electrode is in the button form and covered with cellophane paper. This silver oxide electrode is used as the working electrode and a platinum electrode of 2.5×2.5 cm area as the counter electrode

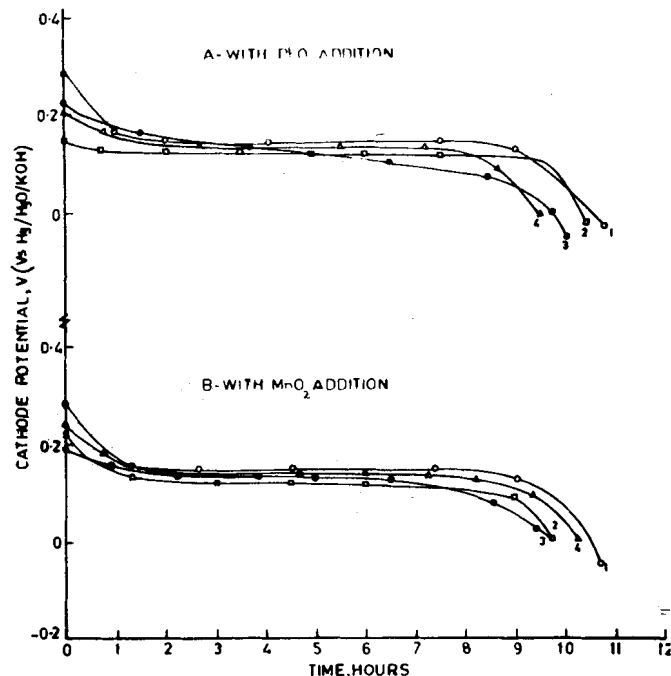


Fig. 1. A. Cathodic reduction of silver oxide (AgO) with lead-dioxide addition
1. Pure silver oxide (AgO) 2. $AgO + 5\% PbO_2$
3. $AgO + 10\% PbO_2$ 4. $AgO + 15\% PbO_2$
B. Cathodic reduction of silver oxide (AgO) with manganese-dioxide addition
1. Pure silver oxide (AgO) 2. $AgO + 5\% MnO_2$
3. $AgO + 10\% MnO_2$ 4. $AgO + 15\% MnO_2$

Luggan capillary of the mercuric oxide reference electrode is kept very close to the working electrode. 100 ml of freshly prepared 40% potassium hydroxide solution is used in all the experiments. The silver (II) oxide electrode is cathodically reduced by impressing constant current of 10 mA from the galvanostat. The potential of the silver (II) oxide electrode with respect to the mercuric oxide electrode is measured. The experiment is repeated with the addition of 5%, 10% and 15% of lead dioxide and electrolytic manganese dioxide. The respective data obtained are plotted in Fig. 1 (A and B).

RESULTS AND DISCUSSION

The investigations are confined to the addition of lead dioxide and manganese dioxide to silver (II) oxide. Since silver (I) oxide gives lower capacity than silver (II) oxide, it was felt desirable to use silver (II) oxide prepared chemically, which however, showed slightly different characteristics than the silver (II) oxide produced by oxidising porous silver plates electrochemically. The chemically produced silver (II) oxide did not show two distinct discharge plateau as usually shown by electrochemical silver (II) oxide [3]. However, it does possess the undesirable feature of discharging from a higher potential.

Experimental data obtained with and without the addition of lead dioxide is presented in Fig. 1A and that of manganese dioxide addition in Fig. 1B. Two important features may be noted in this figure. First that the capacity of cell is maximum without addition of any quantity of lead dioxide. Larger the addition, lower is the capacity. The second most important feature of the effect of addition of lead dioxide is that the initial voltage instantaneously falls to a voltage close to the flat plateau potential. In other words, the cell started discharging from a potential which remains constant for over 75% to 80% of its capacity. This feature is important for several applications where a high energy density and a single plateau potential are the essential requirements. It may however be noted that these discharges are confined to the medium drains at 10 hour rate.

Fig. 1B exhibits similar results as in Fig. 1A with lead dioxide additions. The only difference is that with increase in the quantity of manganese dioxide, there is an increase in capacity of the electrode towards the capacity of the blank electrode. However, in both cases pure silver (II) oxide shows higher capacity than mixed oxide even when the quantity of silver (II) oxide is taken uniformly, viz. 0.3 g/electrode. The most attractive feature of this figure is also the one of instantaneous fall of the voltage of the cell on discharge to the level of flat plateau potential. This feature makes this battery system an attractive one for several sophisticated applications.

The electrodes are made with 0.3 g of silver (II) oxide prepared chemically as mentioned above. From the curve 1, Fig. 1A and B, the operation capacity of the electrode is 105 mAh against the theoretical capacity of 130 mAh. For the same quantity of material, the theoretical capacity in respect of silver (I) oxide is only 70 mAh. From these figures, we find that (a) the discharge occurs at 80% efficiency and (b) one third of discharge should occur at silver (II) oxide stage and the rest of silver (I) oxide stage. Although the electrode exhibits the capacity based on silver (II) oxide state, yet the discharge potential of the curves with additional agents does not start with potential corresponding to silver (II) oxide, giving advantage of high capacity without first potential plateau.

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