

THE LITHIUM-SULPHUR DIOXIDE CELL. I. THE POROUS CARBON BLACK CATHODE

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Summary

The dependence of the specific capacity of carbon cathodes used in Li/SO₂ cells on the cathode thickness and the binder content has been studied. At low c.d. the specific capacity increases with decrease in thickness, while at high c.d. the relation shows a maximum. For cathodes with a thickness above 1 mm the relation between the specific capacity and the c.d. is exponential. The pre-exponent in this relationship is determined by the pore volume and the volume electrochemical equivalent of lithium dithionate. The spatial distribution of the current in the cathode has also been investigated.

Introduction

Earlier publications on the Li/SO₂ cell have considered its behaviour as a function of the discharge conditions and shelf-life [1]. The chemical and electrochemical reactions taking place in the cell under normal discharge conditions have also been studied [2, 3]. It has been shown that the electrochemical balance between the anodic and cathodic components has a considerable impact on the cell safety during overdischarge [4 - 8]. Quantitative data for the effect of the cathodic thickness and the discharge conditions on the performance of the cathodes are available for Li/SOCl₂ cells [9 - 11]. There are, however, only qualitative data for these effects in the case of Li/SO₂ cells. The lack of quantitative relationships explains why the electrochemical balance of Li/SO₂ cells has been calculated by assuming the cathode capacity to be a constant [5, 8].

The aim of the present paper is to assess the specific capacity of porous carbon cathodes in Li/SO₂ cells as a function of the binder content, the thickness, and the rate of discharge, as well as to study the space distribution of the current in the cathode during discharge.

Experimental

Cell

The specific capacity of the cathode was measured in an experimental cell having the inner dimensions of a standard D-cell. Its design, however (Fig. 1), allowed for the cell to be reassembled many times and for the electrodes to be changed. Reliable seals were obtained using flanges and O-rings. A vent on the cell lid was used to introduce the electrolyte solution after assembly of the cell in a dry box. The electrodes were wound tightly together forming a compact core consisting of a lithium foil anode, propylene separator, and a flexible, porous carbon cathode. The length and thickness of the electrodes were determined empirically in such a way that the cell was cathode limited. The electrolyte solution was a 75% mixture of SO_2 in acetonitrile containing 1M LiBr.

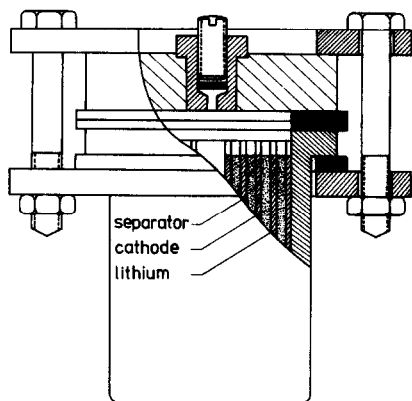


Fig. 1. Experimental cell design.

Cathode

In all cases the cathodes were prepared from acetylene black with 5% Teflon, except for the experiments carried out to assess the effect of the amount of Teflon on the cathode performance. Their initial porosity was always 80%, and the thickness was varied from 0.025 to 0.15 cm. For the study of the current distribution in the cathode a composite cathode was used consisting of 4 similar cathodes, 0.035 cm thick, separated by a propylene separator with a thickness of 0.008 cm. Each separate cathode was pressed on an expanded Al grid with a separate lead isolated from the others.

Circuits

The specific capacity of the test electrodes was determined under constant current discharge. In the study of the spatial distribution of the current in the cathode a branched circuit was employed (Fig. 2) whereby

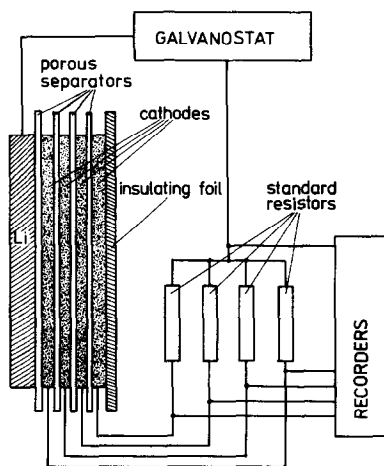


Fig. 2. Circuit for investigation of spatial distribution of the current in the composite cathode.

the total current flowing through the composite cathode was maintained by a galvanostat. The partial current of the separate cathodes was measured by 4 similar, low-ohmic standard resistors (0.01 - 0.002 ohm), and recorded. The standard resistors were so chosen that at current densities of from 1 to 5 mA/cm² the difference in the ohmic drop between any one of them was less than 0.5 mV. This corresponds to less than 1% difference in the polarization of the separate cathodes with regard to the total polarization of the cathode. The cell voltage was also recorded.

Results and discussion

Effect of the binder content

Figure 3 presents the effect of the Teflon content of the cathode mixture on the specific capacity in two cases: for a thin (0.075 cm) cathode at low c.d. (0.5 mA/cm²) and for a thick (0.15 cm) cathode at a medium c.d. (2 mA/cm²). The complete lines denote the capacity with regard to the weight of the active cathode material, while the dotted lines present the capacity with regard to the weight of acetylene black only.

The plots in Fig. 3 reveal that increase of the binder content in the active material leads to a significant decrease in the specific capacity. This effect is, to a small degree, due to the decrease of the active component content (acetylene black) in the cathode material, but is mainly due to the decrease in the specific capacity of the acetylene black itself (the plots with dotted lines in Fig. 3), presumably because of the partial blocking of part of its active surface or plugging of part of the pores of the cathode. Decrease of the amount of Teflon below 5% causes considerable difficulty in cathode preparation and cell assembly, without any significant improvement in cathode performance.

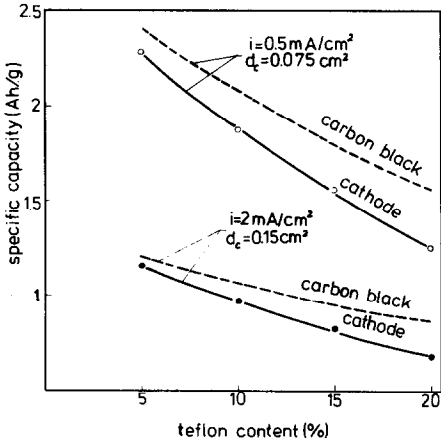


Fig. 3. Effect of the cathode mixture Teflon content on the specific cathode capacity.

Effect of cathode thickness

Figure 4 illustrates the effect of the cathode thickness on the specific capacity at four current densities. The character of the plots is quite different. While at low c.d. the specific capacity falls continuously with increase in cathode thickness, at medium and also at high c.d. there is a maximum. A likely explanation of this maximum is that with decrease of cathode thickness, a favourable state is attained where the cathode operates uniformly

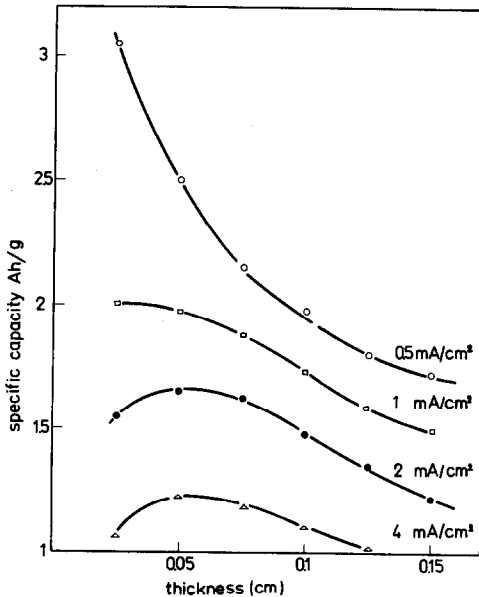


Fig. 4. Effect of the cathode thickness on the specific cathode capacity.

throughout its whole volume. A further decrease in the thickness, however, leads to a decrease in the active surface area and consequently to an earlier passivation at high c.d.

In practical cells for higher current drains the cathodes are thinner and longer, whereby a larger surface area per unit volume is attained. Figure 4, however, clearly shows that increase in the surface area of the cathode by thinning it below 0.05 cm would not lead to any improvement, since the effect of the reduction in the c.d. would be offset by the decrease in the specific capacity.

Effect of the current density

Figure 5 presents the influence of the c.d. on the specific capacity of the cathode at three cathode thicknesses. The dots and full lines correspond to the experimental data, while the dotted lines represent the most probable exponential curves calculated by the least squares method. It is seen that in the case of thick (0.15 cm) cathodes the experimental points fall exactly on the exponential curve. There is only a small discrepancy for medium-thick cathodes (0.1 cm), while for the thin cathodes the discrepancy is considerable. Thus, for cathodes thicker than 0.1 cm the following empirical relation between the specific capacity of the cathode per unit weight, ($A\ h/g$) and the c.d., i , is obeyed:

$$\eta_g = \eta_g^0 \exp(-ki) \quad (1)$$

where k is a constant.

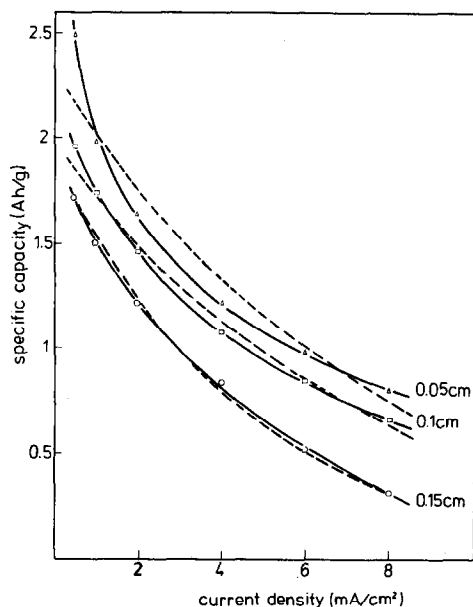


Fig. 5. Effect of the c.d. on the specific cathode capacity.

Figure 6 shows the dependence of the log of the specific capacity of the cathode on the c.d. for cathodes thicker than 0.1 cm. The linearity of these dependencies confirms the finding that eqn. (1) is valid for cathodes thicker than 0.1 cm. It is seen also that the pre-exponent for cathodes thicker than 0.1 cm is 1.92 A h/g, while for 0.1 cm thick cathodes it is somewhat higher, 1.98 A h/g. For thick cathodes the effect of the thickness on the specific capacity appears only in the exponent. The value of the pre-exponent is to be regarded as the maximum sp. capacity at zero c.d., which is independent of the cathode thickness and the c.d.

The physical meaning of the constant η_g^0 can be better understood if we calculate from it the maximum sp. capacity per unit volume of the pores in the cathode, η_v^0 :

$$\eta_v^0 = \eta_g^0 \rho \frac{(1 - P_c)}{(P_c + \epsilon)} \left[\frac{\text{A h}}{\text{cm}^3} \right] \quad (2)$$

where ρ is the real density of the acetylene black, P_c the initial porosity of the cathode, and ϵ is a coefficient accounting for the reduction of the cathode volume.

Experimental values for the cathode expansion during discharge vary from 15 to 30% ($\epsilon = 0.15$ to 0.30) so that the maximum sp. capacity per unit pore volume according to eqn. (2) will be 0.70 - 0.81 A h/cm³. Bearing in mind that the specific volume capacity of the cathode reaction product, Li₂S₂O₄, is 0.77 A h/cm³ [8] it can be concluded that the constant in eqns. (1) and (2) is determined by the pore volume and the volume of the solid reaction product.

The deviation from the exponential dependence, eqn. (1), for thin cathodes, as well as the increase in the pre-exponent with the thinning of the

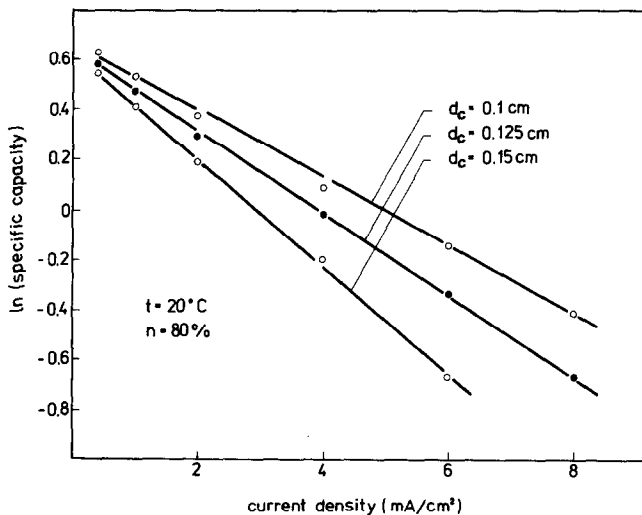


Fig. 6. Dependence of the log of the cathode specific capacity on the c.d.

cathode (Fig. 6), can be explained when one takes into account the fact that with the thinning of the cathode the latter becomes commensurate with the thickness of the porous separator, where a considerable part of the cathodic reaction products can be deposited.

Spatial distribution of the current in the cathode

It might be expected that the distribution of the discharge products in the volume of the cathode in a Li/SO₂ cell is similar to that in a Li/SOCl₂ cell, which has been investigated already [12, 13]. However, it is very likely that the distribution of the products does not follow the current distribution in the cathode.

The measurement of the partial currents during discharge of a multilayer cathode consisting of several thin cathodes, each separated from the other by a thin porous separator (Fig. 2), can provide information on the current distribution through the cathode thickness. Inasmuch as the thickness of the multilayer cathode (0.175 cm) is much smaller than its other dimensions (4 cm wide and 12.5 cm long), it can be assumed that the electrodes are uniformly loaded along the entire surface area, and the spatial distribution of the current will be determined by the current distribution through the cathode thickness. The requirement for a low resistance of the standard resistors (Fig. 2) is equivalent to the requirement that the four separate cathodes are equipotential. The effect of the standard resistors was checked by shorting them one by one for a short time during the discharge. No change in the partial currents was observed.

Figure 7 indicates the change in the partial currents during discharge at 1 mA/cm². In this Figure the separate cathodes are numbered in sequence from the Li anode. The broken line shows the change of the cell voltage. At the beginning the partial currents are equal. There follows a rapid redistribution until the partial currents reach almost steady state values. At the end of the discharge there is a considerable change in the distribution also.

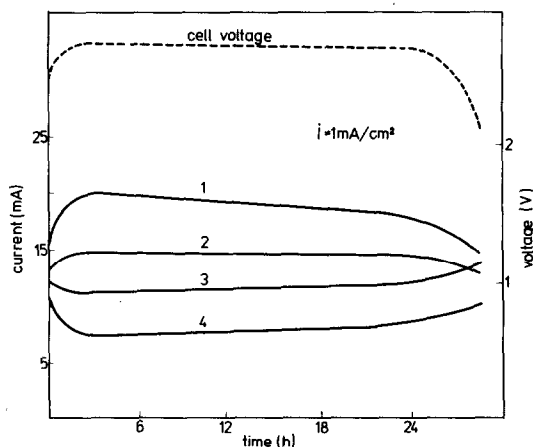


Fig. 7. Spatial current distribution in the composite cathode at 1 mA/cm².

The initial redistribution is presumably due to concentration changes in the volume of the cathode associated with the consumption of Li^+ and the generation of dithionate ions until a steady state condition is attained.

Figure 8 presents the partial current distribution at 5 mA/cm^2 . The picture here is more complicated, and one can discern three characteristic stages: (i) initial distribution stage; (ii) steady state stage; (iii) secondary redistribution stage, comprising the second half of the discharge process. The first two stages are presumably equivalent to those appearing at low c.d., but here the ratio between the partial currents is considerably higher. During the secondary redistribution stage there is a significant decrease in the partial current in the first cathode on account of the rise in the currents of the second, then in the third, and finally in the fourth. At higher rates of discharge part of the electrochemically active surface can be passivated by the generation of relatively small amounts of reaction products, whereby the pores remain partially unfilled with reaction products, while the ionic conduction process is slightly hampered. The occurrence of these events in the first cathode would result in an increase in the load on the other cathodes at the expense of additional voltage drop. The voltage-time curve shown with a broken line in Fig. 8 is in agreement with this assumption. It seems likely that the end of the discharge (low and high rate) takes place, in both cases, when the pores in the frontal surface of the first cathode are plugged with reaction products, thereby ionic transport towards the internal parts of the cathode is seriously hampered.

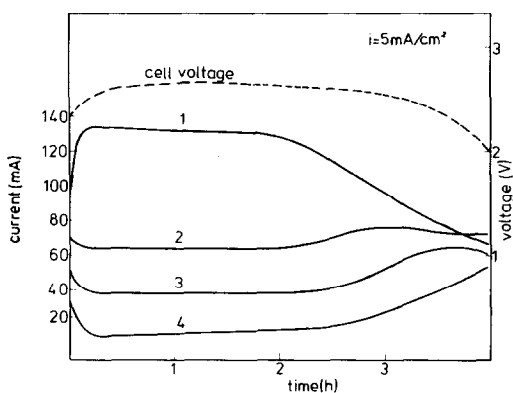


Fig. 8. Spatial current distribution in the composite cathode at 5 mA/cm^2 .

Conclusions

The sp. capacity of the cathode decreases with increase in the binder content (Teflon) not only because of the decrease in the amount of the active component in the cathode mix, but also on account of the partial screening of the active surface and plugging of the cathode pores.

The sp. capacity increases with the decrease of the cathode thickness at low c.d., while at high c.d. there is a maximum in this relationship.

The dependence of the sp. capacity of the cathode on the c.d. is exponential for cathodes thicker than 0.1 cm. At lower thicknesses the exponential character of this dependence is impaired.

The pre-exponent of the above dependence is a constant independent of the discharge rate and the cathode thickness. It is determined by the pore volume and the molar volume of the lithium dithionate.

At low discharge rates, following a short initial distribution the spatial distribution of the current has an approximately steady state character.

At high discharge rates there are three characteristic stages in the spatial distribution of the current: a transient region, an approximately steady state stage, and a stage of secondary redistribution.

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