

THE LITHIUM-SULPHUR DIOXIDE CELL. II. MATERIAL BALANCE

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Summary

On the basis of the condition for optimum cell design, expressions are derived for the determination of the optimum thickness and length of the electrodes as well as of the maximum capacity. There is good agreement between the experimental values and those calculated by the derived expressions. The dependence of the cell capacity on the discharge rate is explained in terms of the relationship between the partial capacities of the separate components and the current. The possibility of an extension of the safe operation range by means of cell optimisation is suggested.

Introduction

Earlier papers have discussed the behaviour of Li/SO₂ cells as a function of the discharge rate and conditions of discharge, and an empirical formula has been derived relating the cell capacity and discharge rate [1]. The chemical and electrochemical processes occurring in the cell operating under normal conditions have also been studied [2, 3].

Later investigations revealed that the balance between the anodic and cathodic materials plays a significant role in the safe range of operation under abuse conditions [4 - 7]. The general opinion is that prepolarization of a cell would result in an explosion if favourable conditions exist for the deposition of Li on the cathode or for the formation of Li-Al alloy on the Al grid of the cathode. It was proved experimentally that anode-limited cells are not liable to explosion [5 - 7]. The component balance in the cells was calculated on the assumption that the specific capacity of the carbon cathode is constant.

In a previous publication it was demonstrated, however, that the specific cathode capacity is a function of its thickness and the discharge rate [10]. Obviously, this dependence should be taken into account when anode-limited cells are to be designed.

It is the aim of this paper to derive expressions for the optimum balance of the cell components which account for the effect of the discharge rate on the specific capacity of the cathode, and which yield maximum capacity and safe operation.

Experimental

All experiments were carried out with special D-size cell cans previously described in Part I of this paper [10]. They allow for reloading with new electrodes and electrolyte after discharge. The electrodes were wound tightly in a spiral. The anode was of Li foil. The cathode material was a mixture of 95% carbon black and 5% Teflon. Initial cathode porosity was 80% and the thickness was varied from 0.05 to 0.15 cm. A polypropylene non-woven separator, 0.012 cm thick, was used. The electrolyte solution was a 3:1 mixture of SO₂ and acetonitrile containing 1M LiBr. The water content of the electrolyte was less than 100 ppm.

Theory

The Li/SO₂ cell capacity can, in principle, be limited by any of the three active components: Li anode, carbon cathode, SO₂ in the solution. The condition for maximum capacity is that the partial capacities of these three components are equal, so that at the end of the discharge there are no unutilized active materials, *i.e.*,

$$Q_a = Q_c = Q_e. \quad (1)$$

The partial capacity of the Li anode can be expressed by:

$$Q_a = k_a \eta_a \cdot \rho_a \cdot d_a \cdot h \cdot l, \quad (2)$$

where η_a is the electrochemical equivalent of Li, ρ_a is its density, and d_a , h and l are the spatial dimensions of the Li anode. k_a is the utilization coefficient of Li, which is practically independent of the c.d. and the thickness, l . Its value depends essentially on the uniform discharge of the cathode, and for a homogeneous cathode it varies from 0.85 to 0.95.

The partial capacity of the cathode can be given by

$$Q_c = \eta_c \cdot \rho_c \cdot (1 - p_c) \cdot d_c \cdot h \cdot l, \quad (3)$$

where ρ_c , p_c , and d_c are the apparent density, the initial porosity, and the thickness of the cathode, respectively. The height, h , and the length, l , are assumed to be equal to those of the Li anode. The specific capacity of the cathode, η_c , is a function of the cathode thickness and the c.d. [10] and should be determined experimentally.

The partial electrolyte capacity is equal to

$$Q_e = k_{SO_2} \cdot \eta_{SO_2} \cdot \rho_e \cdot V_e \cdot C_{SO_2}, \quad (4)$$

where η_{SO_2} is the electrochemical equivalent of SO_2 , C_{SO_2} is its concentration in the electrolyte solution, k_{SO_2} the utilization of SO_2 , and ρ_e and V_e are, respectively, the density and volume of the electrolyte solution. The volume V_e can be expressed by the total cell volume, V_0 , and the volumes of the other components:

$$V_e = k_v \cdot V_0 - k_v \cdot h \cdot l [d_a + d_c(1 - p_c) + 2d_s(1 - p_s)] \quad (5)$$

where d_s and p_s are the thickness and porosity of the separator, respectively. The coefficient k_v takes into account the utilization of the cell volume by the electrolyte and is determined by the need for a free volume for the thermal expansion of the electrolyte solution. Usually its value varies from 0.90 to 0.95 depending on the operating conditions.

The utilization of SO_2 , k_{SO_2} is close to unity. Our own experiments showed that the effect of the cathode thickness and the c.d. on k_{SO_2} is very weak. For c.d. up to 8 mA/cm^2 , and for cathode thicknesses in the range $0.05 - 0.15 \text{ cm}$, all values of k_{SO_2} were between 0.90 and 0.97.

As pointed out above, the maximum capacity is obtained when the partial capacities are equal (eqn. (1)). This equality is actually a system of two equations. Introducing eqns. (2) - (5) in the system of eqn. (1), we can first derive an expression for the thickness of the Li electrode as a function of the cathode parameters:

$$d_a = d_c \frac{\eta_c(1 - p_c)\rho_c}{\eta_a \cdot k_a \cdot \rho_a} \quad (6)$$

and then an expression for the length of the electrodes:

$$l_{\text{opt}} = [V_0/(\rho_c \cdot \eta_c(1 - p_c)d_c \cdot h)] \times \left[\frac{1}{k_a \cdot \rho_a \cdot \eta_a} + \frac{1}{k_{\text{SO}_2} \cdot \eta_{\text{SO}_2} \cdot \rho_e \cdot k_v} + \frac{1}{\rho_e \cdot \eta_c} + \frac{2(1 - p_s)d_s}{(1 - p_c)\eta_c \rho_c \cdot d_c} \right]^{-1} \quad (7)$$

Substituting these magnitudes in eqn. (2) we can obtain the optimum capacity:

$$Q_{\text{opt}} = V_0 \left[\frac{1}{k_a \cdot \rho_a \cdot \eta_a} + \frac{1}{k_{\text{SO}_2} \cdot \eta_{\text{SO}_2} \cdot \rho_e \cdot k_e} + \frac{1}{\eta_c \cdot \rho_c} + \frac{2(1 - p_s)d_s}{(1 - p_c)\eta_c \cdot \rho_c \cdot d_c} \right]^{-1} \quad (8)$$

Inasmuch as the thickness of the Li electrode, d_a , the length of the electrodes, and the respective capacities of the cell Q_{opt} are determined under the conditions of optimum capacity, eqn. (1), all these magnitudes can be considered to have optimum values also.

The thickness of the Li electrode at which its partial capacity is equal to that of the cathode can be determined from eqn. (6).

In eqn. (8), each of the terms in brackets represents the partial volume per unit capacity of the individual components of the cell, respectively, the anode, the electrolyte, the cathode, and the separator.

Comparison of the calculated values of these terms (Table 1) allows assessment of the volume contribution of each of the cell components. The contribution of the separator in eqns. (7) and (8) is introduced through the volume of the separator in eqn. (5). Similarly, the volume of the cathode grid could be introduced into eqn. (5) whereby an additional term will appear in eqns. (7) and (8).

The values of all the parameters appearing in eqns. (1) - (8) and used in all further calculations are presented in Table 2.

TABLE 1

Cathode dimensions (cm)		Partial volumes per unit capacity (cm ³ /A h)					
<i>l</i>	<i>d</i>	Cell	Electrolyte	Anode	Cathode	Separators	Grid
70	0.05	4.267	3.03	0.576	0.245	0.294	0.122
42	0.1	4.122	3.03	0.576	0.281	0.166	0.07
30	0.15	4.127	3.03	0.576	0.333	0.133	0.055

TABLE 2

Notation	Value	Notation	Value
η_a	3.85 A h/g	ρ_c	0.8
η_{SO_2}	0.42 A h/g	ρ_s	0.5
k_a	0.85	C_{SO_2}	0.75 g/g
k_{SO_2}	0.90	V_0	42 cm ³
ρ_a	0.53 g/cm ³	h	4.5 cm
ρ_e	1.31 g/cm ³	k_v	0.90
ρ_c	2.0 g/cm ³	d_s	0.012 cm

Results and discussion

(i) Dependence of the cell capacity on the electrode length

The right-hand side of eqn. (1b) in system (1) can be solved graphically, after substitution of solution (6) of (1a) in (1b), bearing in mind that both sides of eqn. (1b) are functions of the electrode length, *l* (*cf.* eqns. (3) - (5)). The graphical solution of eqn. (1b) allows determination, not only of the optimum electrode length, but also assessment of the dependence of the cell capacity on the electrode length at constant cathode thickness, d_c , and constant cell load (*I*).

The graphical solution of eqn. (1) (Fig. 1) is the common point of the dependences of the partial capacities of the cathode and the electrolyte solution on the electrode length. The cell capacity is limited by the lowest partial capacity, and, consequently, the relationship between cell capacity and electrode length will follow the plot drawn in full lines in Fig. 1. On the right-hand side, this relationship is constrained by the maximum electrode length, which is limited by the cell dimensions. The maximum length of the electrodes wound in a cylindrical cell can be calculated [8] according to

$$l_{\max} = \frac{\pi(R^2 - r^2)}{d_c + d_a + d_s}, \quad (9)$$

where R and r are, respectively, the internal radius of the cell can and the radius of the mandrel around which the electrodes are wound.

The graphical solutions of eqn. (1b) relating the cell capacity and the electrode length can be compared with experimental values obtained for various cathode thicknesses and loads.

Figure 2 shows this relationship for a D-size cell with a 0.1 mm thick cathode for various cell currents. The full lines denote the relationships estimated by eqns. (1) - (5) while the points represent the experimental values. It can be seen that the optimum electrode length increases with the discharge rate and reaches its maximum value limited by the cell radius. The higher discharge rates require the maximum length in order to attain the optimum capacity.

Figure 3 illustrates the dependence of D-cell capacity on the electrode length at a constant load of 750 mA for various cathode thicknesses. At a given current there is an optimum cathode thickness (0.1 cm) at which the maximum cell capacity is reached.

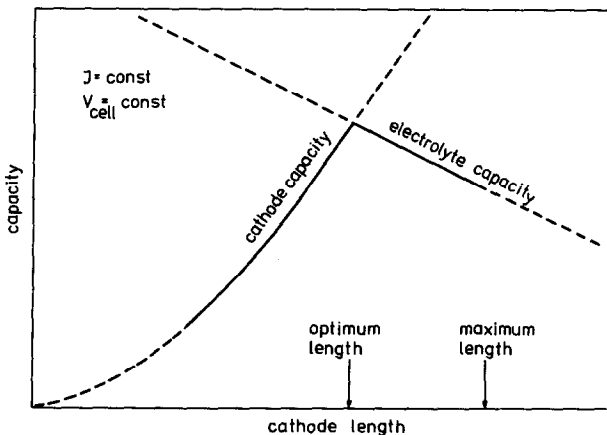


Fig. 1. Dependences of the partial capacities of the cathode and electrolyte solution on the electrode length.

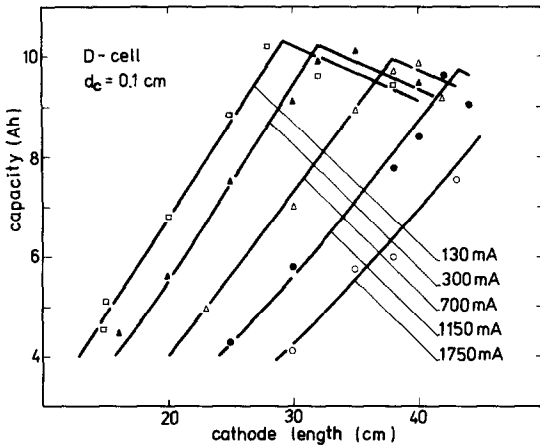


Fig. 2. Dependence of the cell capacity on the electrode length for a D-size cell with 0.1 cm thick cathode.

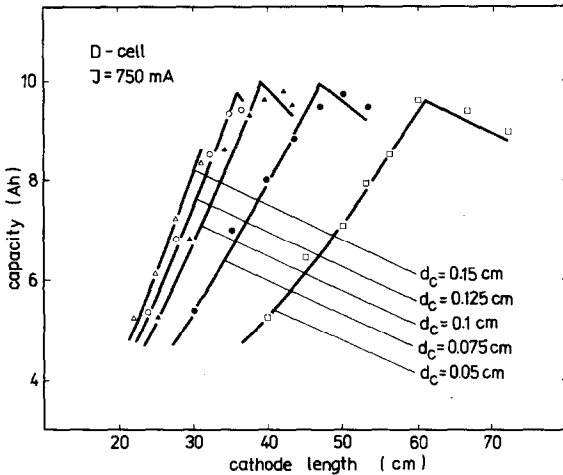


Fig. 3. Dependence of the cell capacity on the electrode length for a D-size cell at a constant load of 750 mA.

The good agreement between the experimental and calculated values (eqns. (1) - (6)) illustrated in Figs. 2 and 3, shows that these equations are reliable for the optimization of Li/SO₂ cells at any predetermined cell size and discharge rate.

Figure 4 shows the maximum capacity of a D-cell, as a function of the cathode thickness, calculated by eqns. (1) - (9) for various discharge rates of practical interest. One can see that there should be an optimum cathode thickness for each discharge rate. Whereas the thick and short cathodes are suitable for the low rates, the long and thin cathodes are appropriate for the high rates of discharge.

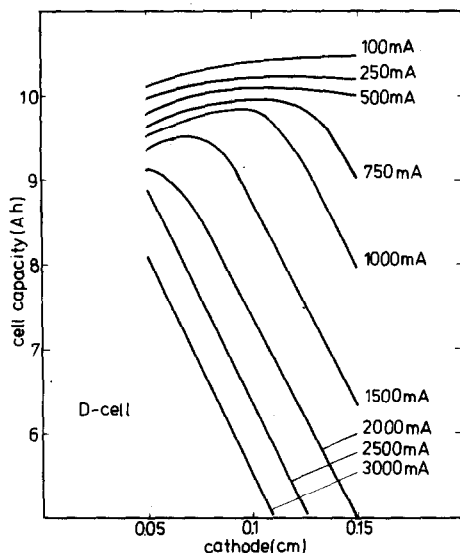


Fig. 4. Maximum capacity of a D-size cell as a function of the cathode thickness for various discharge rates.

At first glance, there is a discrepancy between the results in Fig. 4, showing that for low current drains the optimum capacity is higher for the thicker cathodes, and the results in Part I of the present study [10] where it was found that the specific capacity of the cathodes is higher for the thinner cathodes. Actually, with reduction of cathode thickness and the respective increase in length, we increase the content of inert materials (separator, cathode grid) in the cell, so that the advantage due to the thinner cathode is lost, and a negative effect may result.

As mentioned earlier, Table 1 presents the partial volumes per unit cell capacity of the separate components (anode, cathode, electrolyte solution, separator, cathode grid) calculated for a c.d. of 1 mA/cm^2 for three different cathodes. It can be seen that the partial capacity volumes of the inert materials (separator and grid) in the case of thick and short cathodes is only half the partial volume of the cathode, whereas for the thin and long cathodes, the partial capacity volume of the inert materials significantly exceeds the partial capacity volume of the cathode.

It can be concluded on the basis of the data in Table 1 that the partial capacity volume of the electrolyte solution determines the cell capacity. Remembering the high utilization of the electrolyte solution (above 90%) one can hardly expect any improvement in the capacity of the Li/SO₂ cell.

(ii) Dependence of the capacity on the discharge rate

If the partial capacities are plotted *vs.* the logarithm of the current (Fig. 5), the partial capacities of the Li anode and the electrolyte will be straight lines parallel to the abscissa, since they are independent of the c.d. For an

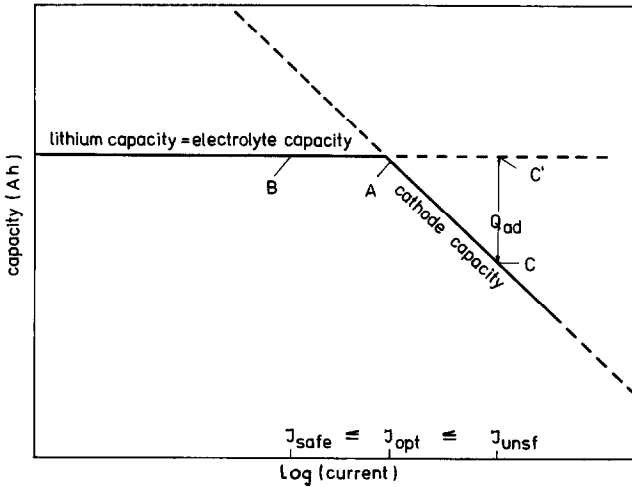


Fig. 5. Dependences of the partial capacities of the cathode, anode, and electrolyte solution for an optimized cell on the exponent of the current.

optimized design the partial capacities are equal and the respective straight lines will coincide. The partial capacity of the cathode is approximately a logarithmic function of the current in the case of thick cathodes and closer to a logarithmic function for thin cathodes ($d_c = 0.1$ cm). Consequently, on semilog coordinates this relationship will appear as a straight line with a positive slope. Accepting that the cell capacity is limited by the lowest partial capacity, the shape of the relationship of the cell capacity *vs.* the current will be that shown by the full line in Fig. 5. The shape of this plot is similar to those found empirically by previous investigators [1, 7, 9].

Figure 6 demonstrates the effect of the discharge rate on the capacity of a cell with a cathode 0.1 cm thick. The cell was optimized at three current drains and, consequently, three different cathode lengths, as shown in the same Figure. The plots are calculated by eqns. (2) and (3) under condition (1) for a given current drain. The points correspond to the experimental data.

Figure 7 presents the capacity of the cell as a function of the discharge rate for cathodes of various thicknesses and lengths shown in the same Figure. The plots are calculated from eqns. (1) - (8), while the points correspond to experimental data. The close agreement between the calculated and experimental relations shows that in the current range where the cell capacity is independent of the current, the capacity is limited by the partial capacity of the Li anode or the electrolyte, while in the current range where there is an exponential dependence between the cell capacity and the current, the cell capacity is limited by the partial capacity of the cathode.

The results presented in Fig. 7 also allow evaluation of the performance of cells optimized for various cathode dimensions, as required by the conditions of operation.

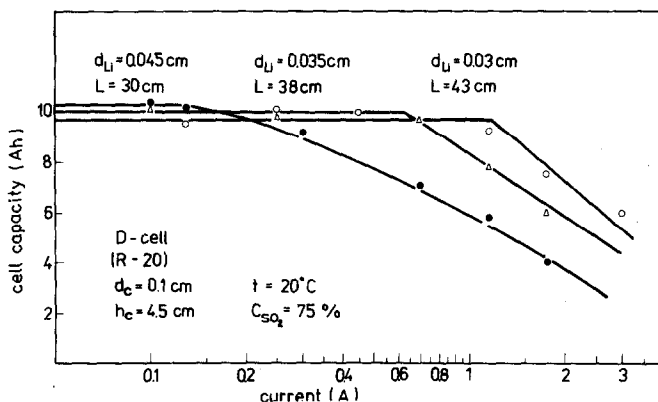


Fig. 6. Effect of the discharge rate on the cell capacity for a D-size cell with 0.1 cm thick cathode optimized at three current drains.

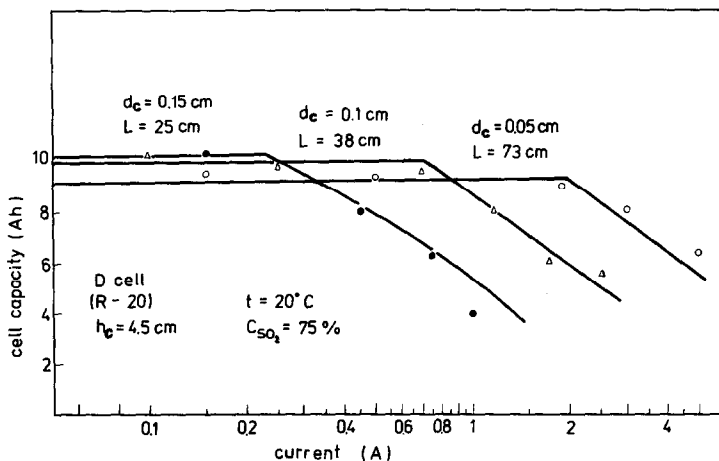


Fig. 7. Effect of the discharge rate on the cell capacity for a D-size cell with cathodes of various thicknesses and lengths.

(iii) Conditions for safe performance of the Li/SO₂ cell

Several authors [4 - 7] have demonstrated that the ratio of the stoichiometric capacities of Li and SO₂ introduced into the cell has a decisive impact on safety under overdischarge conditions. In the case where the partial capacity of the Li anode is lower or equal to that of SO₂, the probability of explosion is very small. It was also shown [4 - 7] that the same is true when the cathode capacity is higher than that of the Li anode. Obviously, a low Li/SO₂ ratio and maximum cathode utilization are desired design features from a safety standpoint. At Li/SO₂ stoichiometric ratios higher than unity, forced discharge leads to voltage reversal and to deposition of Li on the carbon cathode. In the absence of SO₂ in the electrolyte solution a violent reaction between the freshly deposited Li and acetonitrile can occur leading to explosions.

The relationships between the partial component capacities in the cell, the total cell capacity, and the discharge rate (Figs. 5 - 7) allow prediction of the conditions under which Li deposition can take place.

At point A in Fig. 5 the three partial capacities are equal and, consequently, this point corresponds to the current I_{opt} for which the cell is optimized. For currents equal or lower than I_{opt} the cell capacity is limited by the Li anode (point B), so that Li deposition and explosions, respectively, under abuse conditions are excluded. At current drains higher than I_{opt} the cell will be cathode limited (point C), and at the end of discharge there will be an excess of Li capacity equal to the difference between the partial capacities of the anode and the cathode at this point. The conditions for Li deposition on the cathode at voltage reversal are favourable and explosions are likely to occur. Any Li/SO₂ cell, however, can be overdischarged safely only at current drains in the range where the cell capacity is independent of the discharge rate (Fig. 5).

It should be pointed out that the cathode utilization drops with decrease of temperature, so that the range of currents where the cell capacity is rate dependent can be shifted to lower currents (Fig. 5). This explains the decrease of the critical current at which explosions occur on overdischarge when voltage reversal takes place with lowering of the temperature [5 - 7].

Conclusions

A method is presented for the optimization of the design of Li/SO₂ cells. Using this method it has been possible to estimate the optimum capacity of D-cells with cathodes of various thicknesses in the practical range of current drains.

It is shown that the shape of the empirical dependence of cell capacity on current drain can be well explained by the dependence of the partial capacities of the cell components on the discharge rate.

The elucidation of this last dependence enables cell designs to be determined which can safely withstand abuse operating conditions.

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