JOURNAL OF APPLIED ELECTROCHEMISTRY 5 (1975) 313–318

Materials balance in primary batteries. I. Lithium inorganic cells at low discharge rates

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Received 4 October 1974

A study has been made of the design characteristics and optimization procedures leading to an improvement in the maximum cell capacity obtainable with standard size lithium cells at low discharge rates. General relations have been derived between the cell capacity and the porosity of carbon cathode structures at various stages of cell discharge, based on a cell reaction mechanism proposed earlier. A total materials balance relation has been established for the components involved in the cell reaction in cylindrical cells made for a long range application.

Design calculations have been carried out for a typical standard size cylindrical cell. A satisfactory agreement has been achieved between the predicted and the realized performance of cells built according to these calculations.

1. Introduction

Discharge of galvanic cells is often accompanied by a materials redistribution within or between various phases of the system. Whether it is the case of a solid/solid transformation (cathode reduction in alkaline and mercury batteries), a solid/liquid transformation or a combination of both, one should expect a change in the overall density of active materials in the course of discharge. The density changes have not attracted much attention in the past, since in the low energy density cells they are very small relative to the total amount of materials present. With the advent of the high energy density primary systems, however, one is increasingly concerned with the materials redistribution and density changes within sealed cells since these factors dictate the allocation of the available space to active materials and discharge products. This paper deals with one such high energy density system in which a significant volume reduction occurs during discharge, creating some difficulties in maximizing the energy density of sealed cells.

Basic characteristics of lithium/inorganic electrolyte electrochemical systems have been described earlier by Auborn [1] and Behl [2]. The voltage and discharge characteristics of nearly optimized lithium/thionyl chloride cells have been compared to those of other high energy density lithium systems [3]. The performance of standard size cells made with both thionyl chloride and sulfuryl chloride have been described in more detail recently [4].

Two different discharge mechanisms have been proposed for the lithium/thionyl chloride system, one by Auborn, *et al.*:

$$3SOCl_2 + 8Li \rightarrow 6LiCl + Li_2SO_3 + 2S,$$

and one by Behl, *et al.*:

$$4SOCl_2 + 8Li \rightarrow 6LiCl + S_2Cl_2 + Li_2S_2O_4.$$

The discharge products formed by the first mechanism have been positively identified in spent cells, although the stoichiometry of the cell reaction may not have been established with certainty. A good agreement of the calculated cell voltage for this reaction with the measured cell voltage provides a good support for this mechanism.

S_2Cl_2 has not been positively identified in discharged cells. The addition of S_2Cl_2 to the electrolyte prior to discharge raises the cell operating voltage in the first phase of discharge, according to Cogley [5], thus eliminating S_2Cl_2 as a possible

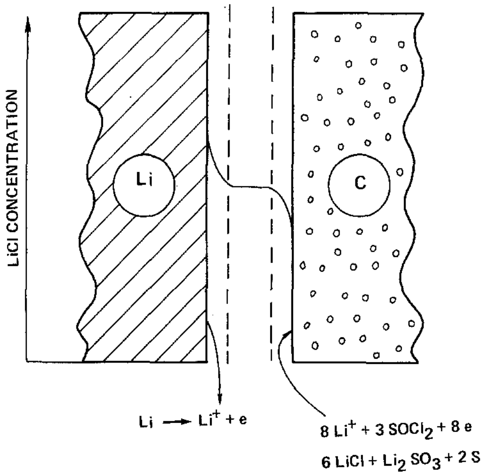

Fig. 1. Schematic presentation of lithium ion concentration gradient in $LiACl_4$ electrolyte in tightly packed cells.

product of discharge. Tests conducted in our laboratories did not show this voltage increase effect in sealed cells. In fact, no effect has been observed of the addition of S_2Cl_2 to the electrolyte other than diluting the electrolyte and reducing the energy density of the system. Since the purification of this compound is not a simple task, it is possible that impurities (such as chlorine or sulfuryl chloride) were present in the S_2Cl_2 in Cogley's experiments in sufficient quantities to support the reaction at a higher operating voltage. The validity of the second mechanism, therefore, remains uncertain at this time.

Both of the proposed mechanisms involve a volume reduction in the course of discharge. A void space grows as the discharge proceeds so that the termination of discharge depends very much on the distribution of the electrolyte residue within the porous cathode structure in the last phase of discharge.

Experiments were carried out to establish where the solid discharge products are deposited. Laboratory cells, made with a large distance between the electrodes, produced a precipitate on discharge, found mostly on or in the vicinity of the lithium electrode. Tightly packed cells, however, continue to operate with a clean lithium surface and a clear electrolyte. All discharge products are precipitated within the cathode pores, producing a hard and fragile cathode of what was initially a flexible soft porous structure.

Good mass transport characteristics of this electrolyte in tightly packed cells could be partially explained on the basis of these experiments as shown schematically in Fig. 1. The absence of the precipitate on the surface of lithium suggests the formation of the supersaturated solution in the vicinity of a dissolving anode by a mechanism probably similar to that experienced with the anodic dissolution of zinc in alkaline electrolyte. The reduction of thionyl chloride on the carbon surface involves the removal of lithium ions from the electrolyte in the formation of the Li_2SO_3 precipitate. Both of these partial discharge reactions result in an increase of the concentration gradient in the solution, driving the transport of lithium ions towards the precipitation sites within the cathode structure.

All the calculations that follow, relating to porosity of the cathode and the capacity at various stages of discharge, are based on the first proposed mechanism.

2. Theoretical

2.1. *Dimensionally stable porous cathodes*

Porous carbon structures are made from a blend of carbon powders, a removable filler and a binder that would preserve the electrode structure upon the removal of the filler in the process of formation of pores. The total volume of all pores within the cathode is a measure of the maximum volume of discharge products formed under most favorable conditions (low rates) without the change in the outside dimensions of the cathode. With a known discharge mechanism, the pore volume V_1 is directly related to the maximum cell capacity Q,

$$Q = k_1 V_1. \qquad (1)$$

The proportionality constant k_1 in Ah cm^{-3} of discharge products formed is calculated from the stoichiometry of the discharge reaction.

The pore volume V_1 could be expressed in terms of the overall cathode volume V and the starting porosity fraction P (cm^3 cm^{-3} of total electrode volume), of which only a fraction ϵ is filled with the discharge products at any stage before the complete discharge:

$$V_1 = \epsilon V P. \qquad (2)$$

From Equations 1 and 2 it follows that:

$$Q = k_1 \epsilon V P, \tag{3}$$

ϵ could be called a choking coefficient, representing a degree to which the pores were filled at any particular stage of discharge.

Each carbon blend used in the fabrication of cathodes shows a limited maximum discharge capacity obtainable at a different maximum discharge rate for each porosity, within certain porosity limits. The total electrode capacity is, therefore, related to the weight of the carbon blend G involved:

$$Q = k_2 G. \tag{4}$$

The proportionality constant k_2 in Ah g^{-1} must be determined experimentally for each type of carbon blend. The weight of carbon contained in a given electrode could be expressed by the volume V and the porosity P of the electrode if the bulk density of the carbon blend d_c (in g cm^{-3}) is measured. The above expression then becomes:

$$Q = k_2 d_c V(1 - P). \tag{5}$$

The starting porosity of the electrode must satisfy both the condition in Equations 3 and 5 for dimensionally stable electrodes:

$$k_1 \epsilon V P = k_2 d_c V(1 - P),$$

or

$$P = \frac{k_2 d_c}{k_1 \epsilon + k_2 d_c}. \tag{6}$$

It is obvious from Equation 6 that the optimum starting porosity is a fixed value at low discharge rates ($\epsilon = 1$) determined only by the experimentally established characteristics of the system k_1 and k_2, and by the bulk density of the carbon blend. If the discharge rate is increased, the electrode will cease to function at some value of the choking coefficient ϵ smaller than unity, depending on the rate. The ϵ-rate dependence has to be determined experimentally before the starting porosity can be selected for discharge rates higher than those yielding the maximum capacity and resulting in a complete choking of electrode pores.

The maximum capacity obtainable from the electrode of size V under the most favorable conditions (low rate and $\epsilon = 1$) follows from Equations 3 and 6:

$$Q = \frac{k_1 k_2 d_c}{k_1 + k_2 d_c} V. \tag{7}$$

2.2. *Dimensional characteristics of cylindrical electrodes*

Design work on cylindrical cells begins quite often with determining the total volume of the cell based on the required operating voltage, and on the total volume available for the finished battery. The next step is the determination of the height/diameter ratio, based on the discharge rate requirements and on the limitations of the assembling technique. Cells made for extremely low discharge rates can be constructed with a wide range of *H/D* ratios, since the ohmic components of the polarization on discharge does not significantly affect the operating voltage of the cell. One begins to be increasingly concerned with the *H/D* ratio, however, when the discharge rates approaches a maximum one, at which the maximum capacity of the cell is still obtainable. In this case the *H/D* ratio must be increased as much as the assembling procedures will allow, since in the concentrical arrangement of cylindrical electrodes of a constant volume, the geometrical surface area of electrodes facing each other increases as the diameter of the electrodes decreases.

The next step in the cell design is the allocation of the cell space to be occupied by the components of the seal, and the void space needed in the cell for the electrolyte expansion. The remainder of the cell interior volume is then available for the active components of the cell.

Lithium inorganic electrolyte cells show a reduction of the volume of active components, as the calculations will show. In order to avoid a formation of bubbles within the electrode structure, an excess of electrolyte has to be provided that will maintain the flooded conditions throughout discharge. Of the two possible choices for placing the extra electrolyte shown in Fig. 2, the second one has an obvious advantage, since it allows the use of electrodes with a higher geometrical surface area. The lithium electrode is placed on the outside of the electrode arrangement for many practical reasons, not least of them being the larger geometrical surface area of this (non-porous) electrode. We now shall proceed to calculate the dimensions of the electrodes for an optimized cell structure of diameter D and volume H.

The excess electrolyte needed to compensate for the volume reduction on discharge (centre hole

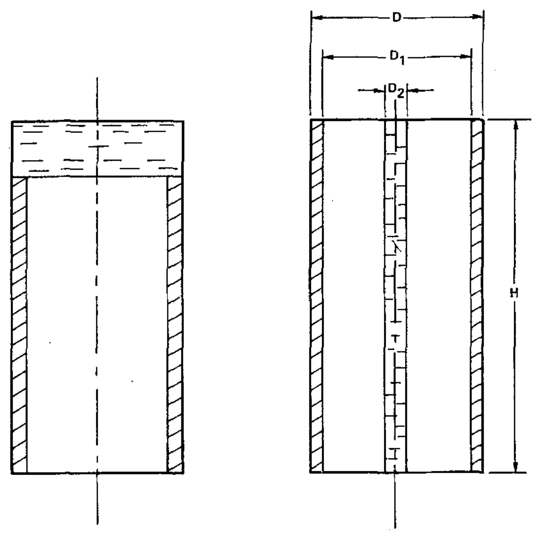

Fig. 2. Choice of arrangements of active materials in cylindrical cells.

of the cathode) is related to the cell capacity:

$$\frac{D_2^2\pi}{4}H = k_3Q, \tag{8}$$

through the specific volume reduction k_3 in $cm^3\,Ah^{-1}$ that is determined by the stoichiometry of the cell discharge and the density of the reactants and products involved.

The overall volume of the cathode is also related to the cell capacity through Equation 3:

$$\frac{(D_1^2-D_2^2)\pi H}{4} = \frac{Q}{k_1\epsilon P}. \tag{9}$$

The volume of the anode is related to the cell capacity in the following manner:

$$\frac{(D^2-D_1^2)\pi H}{4} = \frac{M}{nFd_a}Q\cdot E. \tag{10}$$

where M is the molecular weight of the anode metal, n the number of equivalents mol^{-1} (number of electrons in the discharge reaction), F is a Faraday (26·8 Ah/eq), and d_a the density of the anodic metal. The anode excess factor E has to be determined on the basis of experience. An excess of lithium is necessary in a spent cell not only to ensure a complete utilization of the cathode, but also to continue the cathodic protection of cell hardware against a direct attack by the electrolyte after the cell has been discharged.

The solution of the three Equations 8, 9, and 10 with three unknowns (D_1 D_2 and Q) results in the optimum dimensions of the electrodes, and the cell capacity expressed in terms of the outside dimensions of the active structure. The diameter of the centre hole in the cathode is:

$$D_2 = \left[\frac{nFd_ak_1k_3\epsilon P}{nFd_a(1+k_1k_3\epsilon P)+EMk_1\epsilon P}\right]^{\frac{1}{2}}D. \tag{11}$$

The outside diameter of the cathode (and also the internal diameter of the anode) is:

$$D_1 = \left[\frac{nFd_a(1+k_1k_3\epsilon P)}{nFd_a(1+k_1k_3\epsilon P)+EMk_1\epsilon P}\right]^{\frac{1}{2}}D. \tag{12}$$

The maximum cell capacity is:

$$Q = \frac{nFd_ak_1\epsilon P}{nFd_a(1+k_1k_3\epsilon P)+EMk_1\epsilon P}V \tag{13}$$

with V being the total volume of the active structure.

The thickness of the separator is neglected in this calculation, since it only amounts to 0·1–0·2 mm and does not affect the outcome of the calculations in cells equal or larger in diameter than the AA size.

The constants k_1 and k_3 are the characteristics of the system derived from the stoichiometry of the cell discharge reactions. The constant k_2 is a characteristic of the particular carbon blend and will vary from one case to another depending on the state of the art of making carbon blends to achieve a high specific discharge capacity. Either one of the discharge mechanisms proposed could be tested using the expressions derived here.

3. Experimental

The planning of the experimental program was carried out on the basis of the first discharge mechanism and other expressions derived in Section 2. The density values used in these calculations for starting materials and the discharge products were as follows (in $g\,cm^{-3}$): Li – 0·534; $SOCl_2$ – 1·655; LiCl – 2·068; Li_2SO_3 – 2·10; S – 2·07. The value of k_1 (Equation 1) was calculated to be 1·079 $Ah\,cm^{-3}$ of discharge products.

The value of k_2 (Equation 4) was determined from the tests of cylindrical AA size cells made with highly porous cathodes and with an excess of both Li and $SOCl_2$. The capacity obtained was increasing as the discharge rate was reduced until a further reduction of discharge rate did not result in any increase in the capacity. This limiting value of the cell capacity was found to be 2·266 Ah for a 0·8484 porous cathode of 0·950 g in weight and 3·088 cm^3 in volume. The value of k_2 was calculated to be 2·386 Ah g^{-1}. With the bulk density of the carbon blend used of 2·03 g cm^{-3} the choking factor was calculated from (Equation 6) to be 0·8021. The electrode porosity at the end of discharge ($P - \epsilon P$) amounted to 0·162.

These tests showed that one could not really count on all the available space in the electrode pores to be filled with the discharge product before the electrode ceases to operate. The optimum porosity of the electrode, assuming a complete choking ($\epsilon = 1$ in Equation 6), amounts to 0·818.

A working diagram was constructed in Fig. 3 relating the capacity and the starting porosity of the electrode for the AA size cell discharged to various choking factors.

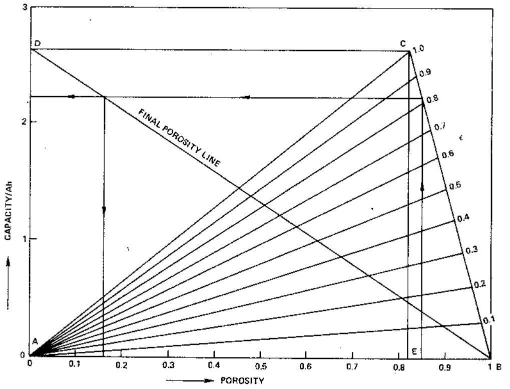

Fig. 3. Cell capacity versus porosity in standard size AA cathode at various states of discharge.

The line AC represents the maximum capacity obtainable with this electrode ($\epsilon = 1$), controlled by the porosity of the electrode. The electrodes of this kind with the porosity lower than 0·818 will cease to operate not because of a lack of active carbon sites but because of a complete plugging with the discharge products of all electrode pores. This causes the lack of electrolyte on the active sites of carbon. If the experiments show that, in fact, the electrode ceases to function already at lower values of ϵ, the corresponding line for that ϵ should be used in estimating the maximum capacity obtainable with these electrodes.

The line BC represents the maximum capacity obtainable with the electrode having a starting porosity above 0·818. These electrodes cease to function not because of lack of electrolyte in the pores but because of lack of active carbon sites. This sort of control of the cell capacity is more favorable in practice for many reasons. It reduces the total weight of the cell (the density of carbon is higher than that of the electrolyte) and it also reduces the costs of production and materials. More importantly, these electrodes are dimensionally stable even at extremely low discharge rates. They yield a higher capacity for the same choking factor since the choking factor apparently dictates the termination of discharge. Different values of ϵ shown along line BC are calculated from Equation 6 for the range of the porosities between 0·818 and unity.

The line BD represents the end porosity as a function of the capacity for any electrode with a starting porosity higher than 0·818, completely discharged. The use of this diagram in determining the pertinent operation parameters is illustrated for the type of cell tested and described earlier in Section 3. Starting with the 0·848 point on the porosity coordinate one simply follows the vertical line up to the intercept with the BC line to read the choking factor on the BC line, reached at the end of discharge. From this point one follows the horizontal line up to the intercept with the capacity realized at the end of discharge. From the intercept of this horizontal line and the final porosity line one turns vertically down to the porosity coordinate to read the end porosity of the discharge electrode.

It is obvious that this procedure is valid only for the dimensionally stable electrodes (of starting porosity higher than 0·818). The porosity of any electrodes, including these, can otherwise be determined at any stage of discharge from the starting porosity P and the choking factor ϵ reached at that state of discharge.

$$Pe = P(1 - \epsilon).$$

The low porosity electrodes were known to expand on discharge at extremely low discharge rates and occasionally deliver a capacity somewhat higher than the AC line for $\epsilon = 1$ will allow, provided there was room between the electrodes to allow such an expression. It is unknown at what stage of discharge the expansion would begin, but the discharge capacity showed the end point above the AC line. This area of expanding electrodes has not been investigated in detail, and for reasons discussed above deserves no attention from a practical standpoint.

4. Conclusions

Several useful conclusions can be drawn from the calculations and the experimental evidence pertaining to the behavior of porous carbon electrodes in the solution of liquid depolarizer – electrolyte at low discharge rates.

(1) There is an optimum porosity of the carbon electrode, made for low discharge rate, that is fixed by the stoichiometry of the discharge reaction and the limiting specific capacity of carbon blend determined experimentally at extremely low discharge rates for the electrodes of extremely high porosity.

(2) There is a need for providing an extra quantity of electrolyte to compensate for the volume reduction of active materials on discharge, in order to avoid bubble formation within the reactive region of the porous structure.

(3) There are two types of failure mechanisms in the operation of porous carbon electrodes for two different regions of the starting porosity of the electrode. The first one is controlled by the electrolyte supply to the pores and the second one by the lack of active carbon sites in the structure.

(4) There is a fixed ratio of electrode diameters in the cylindrical cell and a fixed porosity for each type of carbon blend, that results in the maximum capacity of any given size of cell.

(5) There is a practical graphical way, based on the calculations, for predicting the behaviour of the cathode of any starting porosity. There is, however, only a very narrow region of starting cathode porosities that could be used in building electrodes with no dimensional changes during discharge.

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