JOURNAL OF APPLIED ELECTROCHEMISTRY 6 (1976) 263–268

Materials balance in primary batteries. III. Computer aided design for standard size lithium - thionyl chloride high power cells

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Received 22 May 1975

The study was continued of the design characteristics of high power type batteries made with the lithium/thionyl chloride system. A computer programme flow chart is presented for solving the system of equations correlating all the dimensions of cell components for any selected cell size. Various cell designs are presented for the three standard cell sizes, AA, C and D showing the effect of the geometry of the cell components on the resultant cell capacity. An optimized cell design is suggested for each particular discharge rate required. As a result of the optimization of the electrode structure, a substantial improvement in the maximum cell capacity was obtained with all three cell sizes.

1. Introduction

Part I of this study [1] dealt with the simplest cell construction with concentrically located electrodes. The interdependence was established between various cell parameters in an optimized cell structure. The characteristics of the discharge reaction in lithium/thionyl chloride cells were related to an experimentally established value describing the behavior of porous carbon cathodes.

Part II of the study [2] dealt with the design of the high power type cells made with the wound electrode structures. These cells could be built with various surface areas of the electrodes, depending on the discharge rate requirements. The study correlates the dimensions of cell components with the resultant cell capacity, providing a choice of design solutions to fit each individual power requirement.

Part III, presented here, is an extension of the high power cell studies describing, in more detail, the method of solving the system of equations as well as presenting the results of the design calculations made for three standard size cells. The thicknesses of matched electrodes and separators cover the entire practicable range, reducing the cell design efforts to a direct reading of major cell parameters from the diagrams prepared for each of the three cell sizes.

2. Computation

It has been shown earlier [2] that all the parameters defining the cell structure are determined by a system of nine equations with nine unknowns:

$$L_1 = t\pi n^2 + D\pi n \quad (1)$$

$$L_2 = L_1 + 2t_1\pi n \quad (2)$$

$$L_3 = L_2 + 2t_2\pi n \quad (3)$$

$$L_4 = L_3 + 2t_3\pi n \quad (4)$$

$$t_1 = \frac{Q}{k_2 d_c L_1 H(1-P)} + t_{cs} \quad (5)$$

$$t_3 = \frac{QME}{L_3 HFd_a} + t_{as} \quad (6)$$

$$D = D_c - t(2n - 0{\cdot}5) \quad (7)$$

$$Q = \frac{D^2\pi H}{4k_3} \quad (8)$$

$$t = t_1 + 2t_2 + t_3 \quad (9)$$

whereby, the unknowns were:

L_2 = length of first separator
L_3 = length of anode
L_4 = length of second separator
t_1 = thickness of cathode
t_3 = thickness of anode

t = total thickness (electrodes and separators)
n = number of turns
D = starting diameter (mandrel)
Q = cell capacity.

The values of constants independent of cell size were:

$$k_2 = 2{\cdot}678\ \text{Ah g}^{-1}$$
$$d_c = 2{\cdot}03\ \text{g cm}^{-3}$$
$$P = 0{\cdot}806$$
$$M = 6{\cdot}939\ \text{g equiv.}^{-1}$$
$$E = 1{\cdot}25$$
$$d_a = 0{\cdot}534\ \text{g cm}^{-3}$$
$$F = 26{\cdot}8\ \text{Ah equiv.}^{-1}$$
$$k_3 = 0{\cdot}5643\ \text{cm}^3\ \text{Ah}^{-1}$$
$$t_{cs} = 0{\cdot}0051\ \text{cm}$$
$$t_{as} = 0{\cdot}0035\ \text{cm}$$

The length of the cathode, L_1, is determined prior to computations from the discharge rate requirements for each height of the electrode structure, H, via the maximum cathode current density allowable. In fact, a whole family of L_1 values is entered into the calculation, covering the range of interest resulting in a family of solutions for the same internal diameter of the can, D_c. The thickness of the separators, t_2, is selected on the basis of practical experience with wound cells, the goal being the thinnest separator that is strong enough to withstand handling and also thick and dense enough to prevent internal short circuits in a finished roll.

The flow chart, shown in Fig. 1, summarizes the computer programme devised for the solution of the nine independent simultaneous equations described above.

This programme employs a trial and error approach in order to arrive at a solution, and thereby circumvents the necessity for obtaining a closed solution by tedious algebraic manipulation. In essence, the programme guesses values of n and t and employs these values to calculate the value of a known variable, L_1 (Equation 1). In order to save computer time, the designer defines the range of n and t_1 for which he requires a solution. When the computed value of L_1 (L_{11}), matches the known value (L_1), n and t are real solutions to Equation 1, and may then be employed to calculate the values of L_2, L_3, L_4, t_3, D and Q.

The following description summarizes the steps performed by the programme (see Fig. 1):

1. The values of $n_{\min}, n_{\max}, t_{\min}, t_{\max}, D_c, H$ and t_2 (previously defined) are read.
2. The constants $k_2, d_c, d_a, F, k_3, \pi, P, M$, and E are defined.
3. The values described in (1) are then printed in tabular form for the designer's reference record.
4. The value of L_1 is read (see Fig. 1,D). A list of L_1 values may be entered as data, with the stipulation that the last value equals 0. The latter is accepted as a signal to terminate operation.
5. An initial thickness, $t_1 = t_{1\min}$, is set, as well as Δt_1 (thickness increment) and index, I. The value of Δt_1 is not critical, since the programme has provisions for reducing its magnitude as the solution is approached. The function of the index, I, will be described in steps 8, 11, and 12.
6. The initial number of turns, $n = n_{\min}$, is established.
7. n and t_1 are employed to calculate L_3, t_3, D and t using Equations 2, 3, 6, 8, and 9. The values of D and t are substituted in Equation 7 to determine a new value of n (n_{new}). This value is compared to the previous value of n to test for a possible solution. If n is not equal to n_{new}, ($\leqslant 0{\cdot}01$), then the value of n employed is not a solution, and n is reset to be the average of n_{new} and n (to facilitate convergence). If n is less than $n_{\max}$, the programme then branches to C (Fig. 1) and step 6 is repeated.
8. If n is greater than $n_{\max}$, t_1 is increased by Δt_1 and the new value of t_1 is compared to $t_{1\max}$. If t_1 is less than $t_{1\max}$, n is reset to $n_{\min}$ (by branching to step 5), and a new solution for n is sought. If no solution for n can be found for $t_1 < t_{1\max}$, calculation is terminated, and an appropriate error message: 'No solution in the range of n and t_1' is printed. The execution branches to step 3 where the next value of L_1 is read.
9. If n_{new} is equal to n [$(n_{\text{new}} - n) \leqslant 0{\cdot}01$], then a possible real solution is tested by calculating a value for L_1, (L_{11}) from Equation 1, and comparing this value with the actual value of L_1. Index I is reset, and $n(I)$ and t_{11} (I) are set equal to n and t_1, respectively.
10. If $L_{11} = L_1$, ($L_{11} - L, \leqslant 0{\cdot}01$), Q, L_2, and

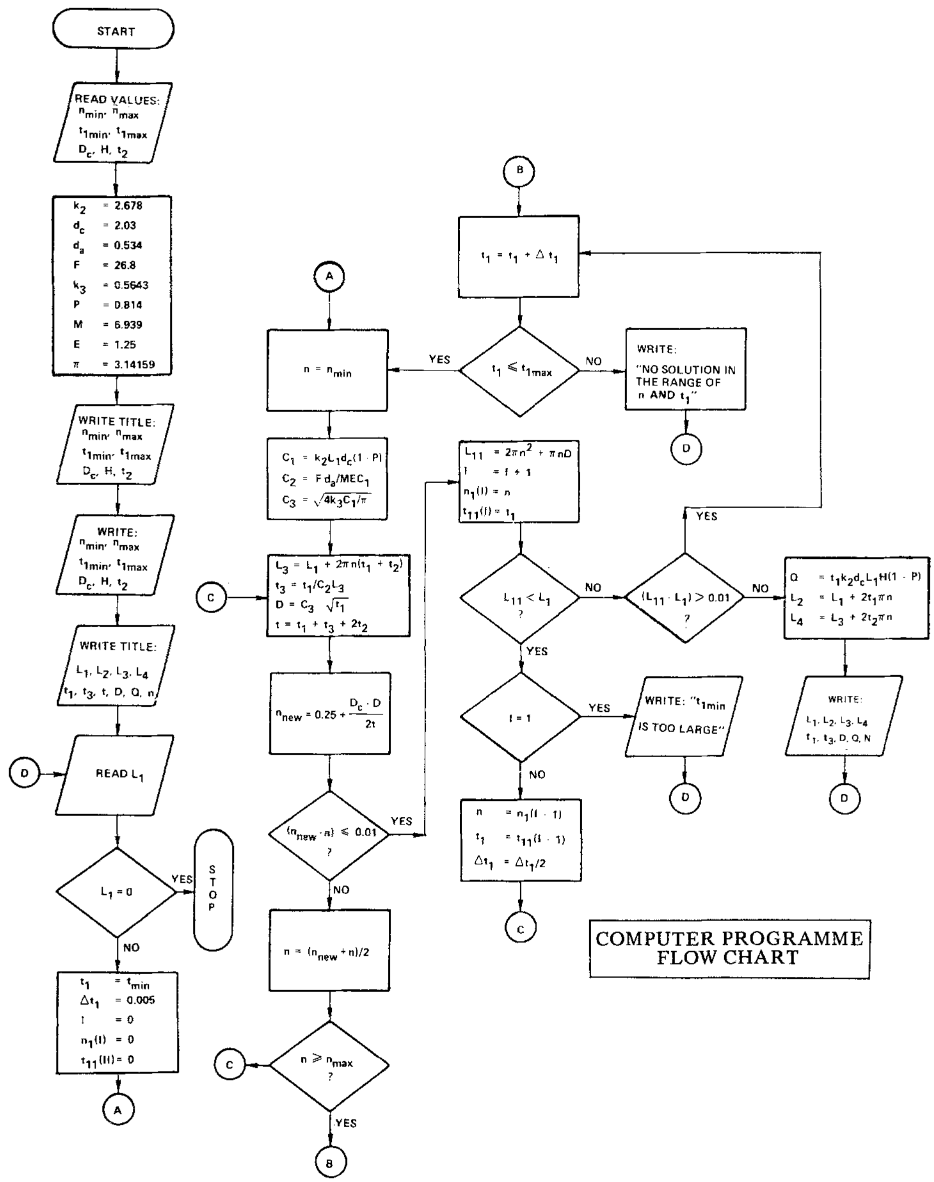

Fig. 1. Computer programme flow chart.

L_4 are calculated for Equations 5 and 4, respectively and the values of $L_1, L_2, L_3, L_4, t_1, t_3, t, D, Q$, and n are printed in tabular form. Execution branches to step 3, where the next value of L_1 is read.

11. If L_{11} is greater than L_1, then t_1 is increased by Δt_1, and execution (if $t_1 \leq t_{1\,max}$) branches to step 5, where n is reset to n_{min} and a new solution for n is sought for this value of t_1. Execution is terminated if $t_1 > t_{1\,max}$, with the appropriate error message: 'No solution in the range of n and t_1.' (This error message is employed when either n or t_1 exceeds the maximum value n_1 or t_1, respectively). Execution branches to D, Fig. 1 (Step 3) for the next value of L_1.

12. If $L_{11} < L_1$, and if $I = 1$, then $t_{1\,min}$ was chosen at too large a value. Calculation terminates with the printing of the error message, '$t_{1\,min}$ is too large', and execution branches to D, Fig. 1 (Step 3), for the next value of L_1.

13. If $L_{11} < L_1$, and if $I \neq 1$, then the previous value of L_{11} was greater than L_1. n_1 and t_1 are

Table 1. Typical computer printout for C size cell

L_1 (cm)	L_2 (cm)	L_3 (cm)	L_4 (cm)	T_1 (mm)	T_3 (mm)	T (mm)	D (cm)	Q (Ah)	N –
12·00	14·20	14·40	14·59	1·69	0·91	2·89	1·24	7·77	2·08
14·00	16·14	16·37	16·60	1·39	0·77	2·45	1·21	7·40	2·46
16·00	18·09	18·36	18·63	1·17	0·66	2·13	1·19	7·07	2·85
18·00	20·05	20·35	20·65	1·01	0·58	1·89	1·18	6·84	3·22
20·00	22·00	22·35	22·69	0·88	0·51	1·70	1·16	6·59	3·61
22·00	23·97	24·34	24·72	0·78	0·46	1·54	1·14	6·38	3·99
24·00	25·93	26·34	26·76	0·70	0·41	1·41	1·13	6·16	4·39
26·00	27·89	28·34	28·79	0·63	0·38	1·31	1·12	5·97	4·77
28·00	28·86	30·34	30·83	0·57	0·34	1·22	1·10	5·79	5·16
30·00	31·83	32·35	32·87	0·52	0·32	1·14	1·09	5·61	5·55

$Dc = 23{\cdot}0$ mm, $H = 37{\cdot}5$ mm, $T_2 = 0{\cdot}2$ mm.

reset to their previous values, $[n_1(I-1)$ and $t_1(I-1)]$, and the increment of Δt_1 is reduced by a factor of 2. Execution then branches to C, Fig. 1, (or step 6).

Reducing the increment, Δt_1, in this fashion results in the desired effect of approaching the real solution from one direction, by first taking coarse steps, and successively reducing the size of the steps until the desired accuracy is met $[(L_{11} - L_1) \leqslant 0{\cdot}01]$. If the value of L_1 is exceeded $(L_{11} > L_1)$, this is used as a test to indicate that the t_1 was increased in too large a step. As a result, t_1 is reduced, and n and t_1 are reset to their previous values to insure that $L_{11} > L_1$. This procedure is employed to insure that L_{11} does not overshoot the value of L_1.

3. Results and discussion

The computer programme discussed in the preceding section was arranged in such a way that includes the characteristics of this electrochemical system (k_3 is entered directly and k_1 is included in the porosity, P) and also the characteristic of the particular cathode material (k_2). Only the cell size (D_c and H) and the thickness of the separator (t_2) have to be selected before the programme can be run for any practicable length of the cathode. A typical computer printout is shown in Table 1 for the C size cell. The internal space of the cell can, available for placing the electrode structure (D_c, H), has been determined after space was allocated inside the standard size C can for the components of the cell seal. The separator thickness of 0·2 mm

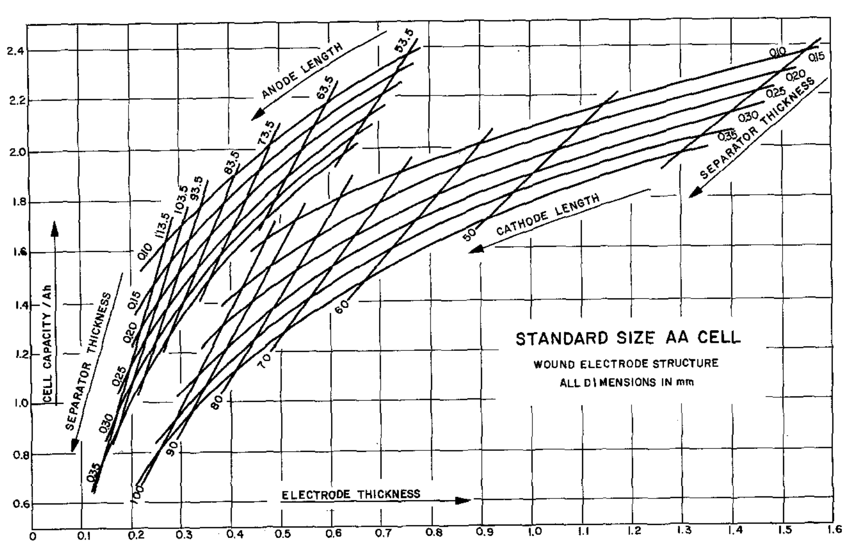

Fig. 2. Cell capacity versus electrode dimensions standard size AA cell.

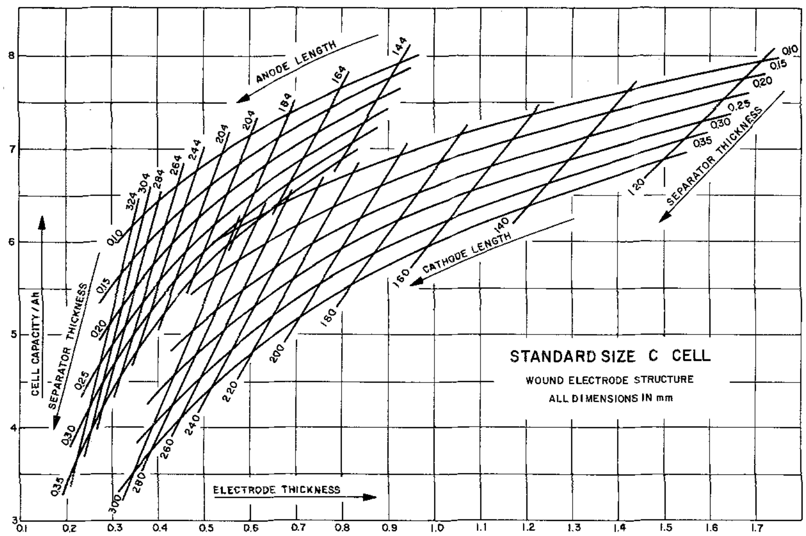

Fig. 3. Cell capacity versus electrode dimensions standard size C cell.

was selected to illustrate the structure of the most common electrode package. Various size cathodes were selected covering the range of interest (column L_1) before the programme was run. All other cell parameters were printed in the same order in which they are shown in Table 1.

The lengths of all four components in the wound electrode structure must be different, increasing in the order in which they first appear when viewed from the hollow center of the wound structure. The cathode was the shortest member in this particular arrangement [2]. Cathodes outside this length range could be selected, but the corresponding thicknesses (t_1) would fall out of the range practicable with the present state-of-the-art of making these electrodes. Table 1 clearly indicates the decrease in the cell capacity (Q) as the cathode length (L_1) is increased, since longer cathodes require more inert materials (separators, current collectors) in the same volume available for placing the finished electrode package. The size of the mandrel (D) is directly proportional to the cell capacity as expected. The last column in Table 1 represents the number of turns made around the mandrel with the stack of matching electrodes and separators. For practical reasons, the wound cells

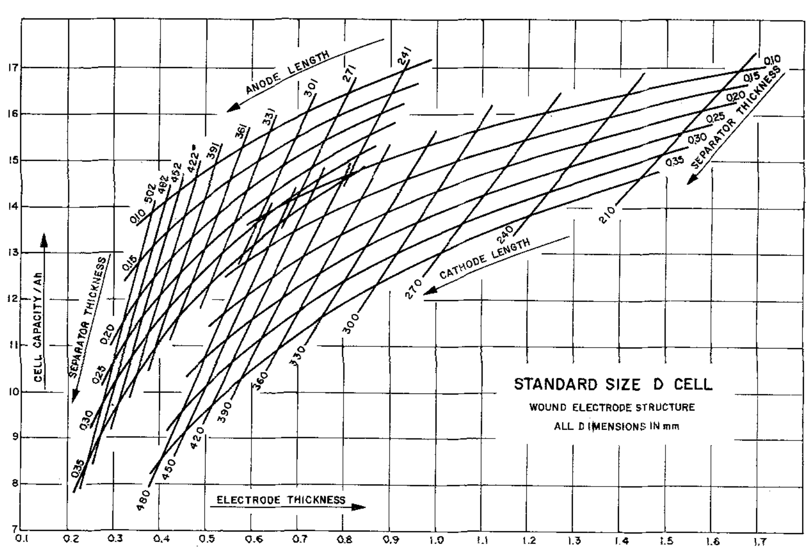

Fig. 4. Cell capacity versus electrode dimensions standard size D cell.

are rarely made with less than two complete turns. The entire calculation becomes absurd when the number of turns falls below 2 and begins to approach 1, since the wound cell with $n = 1$ yields lower capacity than the concentric electrode structure discussed earlier [1]. Further increase in the cathode length would result in a rapid reduction in the cell capacity, since the cathode thickness must be reduced. The limiting case in this direction is, obviously, the cell structure with zero capacity (two separators and two current collectors rolled together with no lithium and no carbon).

Computations were carried out for three standard size cells covering the entire practicable range of cathode sizes and for six different thicknesses of separators. Figs. 2 and 3, and 4 represent the cell capacity as a function of the electrode thickness in a matched electrode structure for the standard AA, C and D size cell, respectively.

The optimization of the standard size cells begins either by specifying the cell capacity or the cell rate capability or (more often) both. A quick look at the diagrams will show the dimensions of the electrodes required to meet the performance specification. The electrode dimensional characteristics for the C size cell in Table 1 are represented with the 0·20 mm separator thickness line in Fig. 3. Two parts of the diagram represent, separately, the cathode and the anode characteristics. The matched pairs of electrodes are defined by the intersection of the cell capacity line with the selected separator thickness line shown for each electrode. The calculation is based on the assumption that both separators are of the same thickness and there is no practical reason to construct the cell otherwise. One should therefore proceed from the cathode defining point horizontally (constant capacity line) to the intersection with the same thickness separator line in the anode region of the diagram to find the anode defining point. The electrode length scale is, obviously, not linear and the points between the lines indicated must be determined by interpolation. The lines representing constant cathode thicknesses are accurate values. However, since the difference in the anode and the cathode length depends slightly on the thickness of the separator used, the lines representing the constant anode length may be up to ± 3% in error from one extreme of the separator thickness range to the other. This is considered satisfactory for graphical presentation. Accurate numbers are obtained when the computation is carried out for each pair of matched electrodes. The part of the diagram representing the extreme electrode lengths is omitted (lower left hand corner). Although it would be of no practical use, it is interesting to note that, if extended, it would end on the zero capacity line. All the electrode thickness lines converge to a point at the zero capacity line representing the equivalent thickness of the current collector screen used in each of the electrodes. (For the purpose of simplifying the calculations the equivalent thickness of the screen is defined as the thickness reached when the screen of the fixed apparent area is rolled into a foil). In practice, however, the electrodes could not be made with the thickness lower than the apparent thickness of the screen used.

The diagrams enclosed could be used directly for a quick determination of the cell design for each particular performance requirement, assuming the same characteristics of the cathode blend (k_2). With any other characteristics of cathode blend or for any other size of the cell a complete programme has to be run to arrive at the electrode parameters of the optimized cell.

References

[1] N. Marinčić, *J. Appl. Electrochem.* 5 (1975) 313–318.
[2] *Idem, ibid* 6 (1976) 415–422.