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Materials balance in primary batteries.
II. Lithium inorganic batteries at high discharge rates

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A study was continued of the design characteristics and optimization procedures leading to an improvement of the maximum cell capacity obtainable with the high power type lithium inorganic batteries. The general relations derived for the low power type cells have been modified for use in the design of the high power type cells. A materials balance was established for the interior components of cylindrical cells made for high discharge rates.

Design parameters were calculated using a computer program for several sizes of cylindrical cells. A satisfactory agreement was reached between the predicted and the realized performance of the cells built with the calculated design parameters.

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1. Introduction

Lithium inorganic batteries have been described in detail in several recent publications. Characteristics of the lithium inorganic battery systems have been discussed by Auborn [1] and by Behl [2]. The voltage and the discharge characteristics of finished cells have been compared with the characteristics of cells of the same size made with the lithium/organic electrolyte systems [3]. The performance of the standard size lithium inorganic cells has been described in more detail recently [4].

A materials balance study has been made [5] of the low power cylindrical cells made with the lithium/thionyl chloride system. The cell design calculations were based on the stoichiometry of the cell discharge reaction and also on the experimental work characterizing the behaviour of the porous carbon cathode used in these cells. The following were the basic parameters established in those studies.

(1) The specific cell capacity (k_1) obtained per unit volume of the reaction products formed on discharge was calculated to be 1·079 Ah cm^{-3}. This parameter is a characteristic of the lithium/thionyl chloride system and is independent of the cell construction.

(2) The maximum specific cell capacity (k_2) obtained per unit weight of the carbon blend was determined experimentally for cylindrical cathodes operating at low discharge rates and high porosities. This parameter was found to be 2·386 Ah g^{-1} for the carbon blend used in this particular electrode configuration. This is a characteristic of the electrode configuration in the cell made with a given electrochemical system. These measurements had to be repeated for high power type electrodes in order to establish the value of this parameter applicable in describing the behaviour of the high power cells.

(3) The specific volume reduction in the course of discharge (k_3) was calculated from the stoichiometry of the discharge reaction and the densities of the reactants and products. It was found to be 0·5643 cm^3 Ah^{-1}. It is another characteristic of the electrochemical system, independent of the cell construction or the discharge rate.

The new value of the maximum capacity obtained with the high power type electrodes, combined with the basic relations established for the low power electrodes, made possible the development of the design procedures leading to the optimized electrode structures for the high power cells.

2. Theoretical

2.1. *The geometry of the wound electrode structure*

The high power type cells are usually made with the wound electrode structure. This is particularly convenient in cases when the cylindrical shape of the cell must be preserved while the surface area of the electrodes is being maximized. The high power type cells must be made with a maximized surface area of electrodes, because of the relatively low conductivity of the electrolytes used. The geometry of the wound electrodes had to be examined before any optimization attempt was made. In order to establish the relation between the dimensions of individual electrodes and the dimensions of the finished roll, one should first consider a simple spiral shown in Fig. 1.

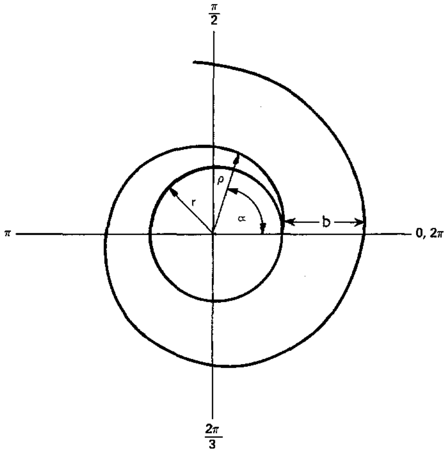

Fig. 1. Geometry of spiral winding.

The spiral originates on the perifery of a round mandrel of radius r, used to start the winding of the electrode package. The basic characteristic of this spiral is a constant gain in the distance of a point on the spiral from the centre of the mandrel with each completed turn. The distance ρ can be expressed in terms of the number of turns n and the increase of the distance from the centre with each turn, t,:

$$\rho = r + nt. \tag{1}$$

The length of the spiral, L, can be expressed in terms of the distance ρ and the angle α involved.

With $\alpha = 2\pi n$ and Equation 1, one obtains:

$$L = t\pi n^2 + 2r\pi n. \tag{2}$$

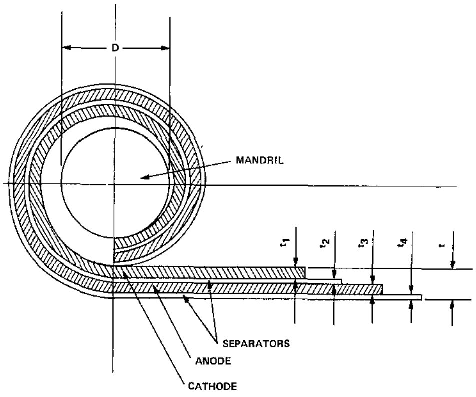

Fig. 2. Winding of the electrode structure.

Fig. 2 shows the relative positions of the two electrodes (cathode and anode) and the two separators during the winding operation. It is obvious that all four components have to be of different lengths in order to properly match the electrode surfaces in a finished roll. With the known thicknesses of all four components and the radius of the mandrel one can calculate the individual lengths required to complete each given number of turns in the roll:

Cathode	$L_1 = t\pi n^2 + 2r\pi n$	(3)
First separator	$L_2 = t\pi n^2 + 2(r + t_1)\pi n$	(4)
Anode	$L_3 = t\pi n^2 + 2(r + t_1 + t_2)\pi n$	(5)
Second separator	$L_4 = t\pi n^2 + 2(r + t_1 + t_2 + t_3)\pi n.$	(6)

The minimal diameter (D_c) of the can required for containing the finished roll can be calculated as follows:

$$D_c = \rho_n + \rho_{n-0\cdot 5}$$

or with Equation 1

$$D_c = 2r + t(2n - 0\cdot 5). \tag{7}$$

2.2. *Cell design procedures*

Various design procedures have been employed in this work, depending on the definition of the cell requirements. The most common one is described here, starting with the fixed cell capacity, resulting from the discharge required over a fixed period of time.

For reasons discussed earlier [5], lithium cells are designed with a cathode-controlled maximum capacity. Therefore, the dimensional characteristics of the cathode must be established before the other components in the electrode structure are defined to insure the proper performance of the controlling electrode. Assuming that the value of the maximum capacity of the carbon blend, k_2, (Ah g^{-1}) has been determined experimentally for the high power type electrodes, the optimal porosity of the carbon structure can be calculated as follows:

$$P = \frac{k_2 d_c}{k_1 \epsilon + k_2 d_c} \tag{8}$$

with ϵ being the choking factor and d_c the bulk density of the carbon blend. The total volume of the carbon structure required for the cell having a capacity Q (in Ah) is calculated next:

$$V_c = \frac{Q}{k_1 \epsilon P}. \tag{9}$$

The surface area of the cathode has to be estimated from the maximum discharge current density established in the process of determining the value of k_2. The discharge current density has to be maintained below the value at which the cathode begins to deliver less than the maximum capacity. The height of the wound electrode structure, H, is determined from the chosen height of the finished cell, and it is identical with the width of the electrode before winding. The cathode length and the thickness of the carbon structure are then easily calculated from the volume, the surface area and the width of the cathode. The total thickness of the finished cathode is obtained by adding to the thickness of the carbon structure the equivalent thickness of the current collector screen used to make the cathode. This, in turn, is calculated from the density of the screen metal and the weight of the screen per unit of its geometrical surface area. Thus, with a completely defined cathode, one can proceed to design the other cell components.

The cylindrical space in the centre of the roll is needed to store the extra electrolyte that will compensate the volume reduction on discharge and, with adequate wetting characteristics of the cathode and the separator, prevent the formation of bubbles within the electrodes. This space can be formed by winding the electrode structure around a mandril which is needed, anyway, for starting the winding operation. Since the volume of the extra electrolyte is determined by the capacity of the cell Q, the diameter of the mandril D can be calculated as follows:

$$D = \left(\frac{4k_3 Q}{\pi H}\right)^{\frac{1}{2}}. \tag{10}$$

The volume of anode required to balance the cell capacity Q with excess factor E would be:

$$V_a = \frac{ME}{nFd_a} Q + V_s \tag{11}$$

where M is the atomic weight, n the number of equivalents per gram atom, and d_a the density of the anode metal. Anodes are made by impressing a nickel or a steel screen into a lithium foil. The screen reinforces the anode structure and acts as a current collector that improves the utilization of metallic lithium. To the volume of lithium must be added the volume of the screen V_s used as the anode current collector. Although the volume and the width of the anode will thus be known, the thickness of the anode cannot be calculated since its length depends on its position in the sandwich and on the thicknesses and the lengths of the cathode and separators. However, the volume of the screen could be determined at this time by choosing a screen of the same surface area as the one used in the cathode. This will mean that a section of the anode is not going to be matched with the screen, but that can be tolerated, since the last turn of the anode faces the cathode on one side only. The total thickness and the length of the anode are going to be entered as unknowns in one of the equations defining the geometry of the electrode structure.

The following are, therefore, the parameters that are determined before the final matching can be made of the electrodes and the separators in the wound electrode structure:

Cathode length: L_1

Cathode thickness: t_1

Cathode width: H

Anode volume: V_a

Separator thickness: t_2

Mandrel diameter: D.

With the parameters defined so far, the geometrical matching of the electrodes and the separators in the wound structure can be achieved by solving the following set of equations:

Cathode length: $L_1 = t\pi n^2 + D\pi n$ (12)

First separator length: $L_2 = L_1 + 2t_1\pi n$ (13)

Anode length: $L_3 = L_2 + 2t_2\pi n$ (14)

Second separator length: $L_4 = L_3 + 2t_3\pi n$ (15)

Anode thickness: $t_3 = \frac{V_a}{Ht_3}$ (16)

Total thickness: $t = t_1 + 2t_2 + t_3$. (17)

The solution of the above six equations for the six unknowns (t, n, L_2, L_3, L_4 and t_3) will complete the list of dimensions defining all four components in the wound cell structure. With a simple rearrangement the five unknowns could be expressed in terms of the sixth, the number of turns:

$$t = \frac{L_1}{\pi}\, n^{-2} - Dn^{-1} \tag{18}$$

$$L_2 = L_1 + 2t_1\pi n \tag{19}$$

$$L_3 = L_1 + 2(t_1 + t_2)\pi n \tag{20}$$

$$L_4 = L_1 - 2D\pi + 2L_1 n^{-1} - 2t_2\pi n \tag{21}$$

$$t_3 = \frac{L_1}{\pi}\, n^{-2} - Dn^{-1} - t_1 - 2t_2 \tag{22}$$

$$t_3 = \frac{V_a}{H[L_1 + 2(t_1 + t_2)\pi n]}\,. \tag{23}$$

The number of turns, n, is calculated by combining the Equations 22 and 23. A cubic equation results of a general form:

$$n^3 + pn^2 + qn + r = 0 \tag{24}$$

where

$$p = \frac{L_1(t_1 + 2t_2) + 2D(t_1 + t_2) + V_a/H}{2\pi(t_1 + t_2)(t_1 + 2t_2)} \tag{25}$$

$$q = \frac{L_1 D - 2L_1(t_1 + t_2)}{2\pi^2(t_1 + t_2)(t_1 + 2t_2)} \tag{26}$$

$$r = -\frac{L_1^2}{2\pi^2(t_1 + t_2)(t_1 + 2t_2)}\,. \tag{27}$$

There is only one real and positive root of the above equation for any realistic set of constants chosen on the basis of the characteristics of the system (k_1, k_2 and k_3). With the known value of the number of turns, n, one can go back to the Equations 18–22 and calculate the rest of the parameters of the electrode structure.

A computer program has been set up for the above calculations which provides a quick solution for all the cell parameters once the input data are prepared for each desired cell size.

3. Experimental

3.1. *Characterization of carbon cathodes*

Of the three characteristics of a liquid depolarizer electrochemical system, k_1, k_2 and k_3 (see Introduction), two (k_1 and k_3) are determined by the stoichiometry of the cell discharge reaction and are not related to any particular cell design. The remaining one, (k_2 in Ah g^{-1}) had to be determined experimentally for each type of cathode structure used. These tests must be carried out on cathode deficient cells so that the cathode capacity could be determined at each of the selected discharge rates with all other active components present in excess of the amounts involved in discharge.

The standard size AA cell was selected as a test vehicle. The wound electrode structure was made using a 0·030 in.* thick sheet cathode, 1 x 2 in. in size, combined with a 0·015 in. thick lithium anode, 1·5 x 3 in. in size. The electrodes were separated with 0·005 in. thick nonwoven glass sheet. The cells were filled to capacity with the electrolyte,

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* 1 in ~ 2·54 cm.

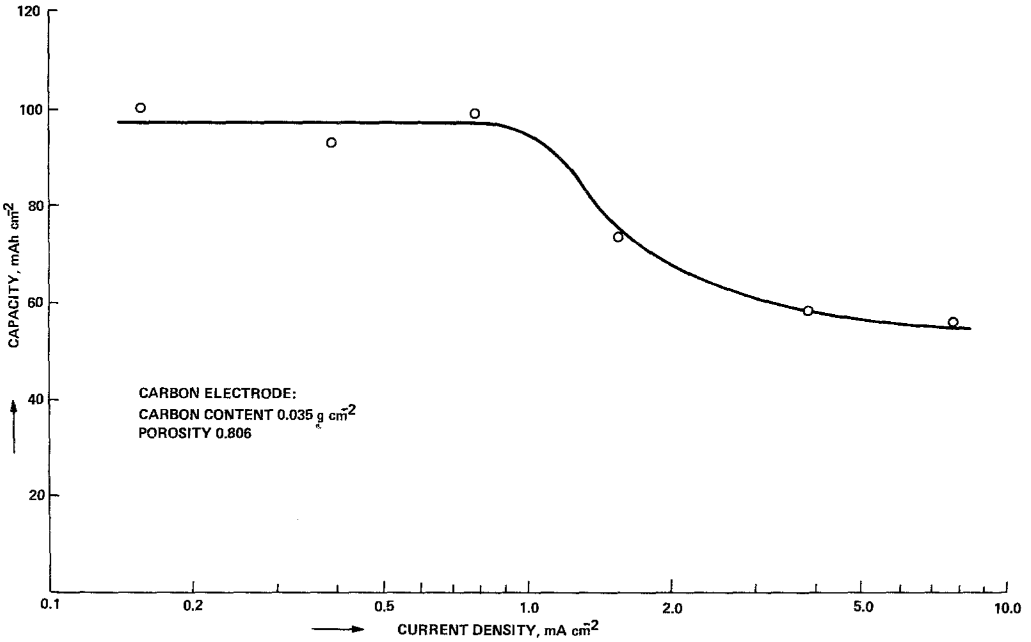

Fig. 3. Capacity-rate diagram for thin cathodes.

sealed and placed on a continuous discharge test. The custom made test equipment provided a constant current and an automatic voltage cut-off both individually controlled, for each test station. The capacity obtained to a 3·0 V cut-off is represented as a function of the discharge current in the diagram in Fig. 3. This diagram shows that the maximum cell capacity is obtained at approximately 1·25 mA cm^{-2}, and a further reduction in the discharge rate does not result in an increase of the capacity. This maximum value is a fixed characteristic of this type of cathode and could be extrapolated within wide limits in designing cells of various sizes for use at the discharge current densities equal or lower than the above. The cells made for use at higher current densities must be designed using the corresponding maximum capacity, taken from the above type of diagram for the same type of cathodes.

The cathodes used in these tests had the carbon porosity of 0·806 and contained 0·035 g of the carbon blend per each cm^2 of the surface, or 2·678 Ah g^{-1} of the carbon blend. The thickness expansion during discharge was found to be 32% of the starting value.

With a value of k_2 of 2·678 Ah g^{-1} and k_1 equal to 1·079 Ah cm^{-3}, the choking factor, or in this case the expansion factor, was calculated for Equation 8 to be 1·212. This would suggest only 21·2% cathode expansion assuming zero porosity at the end of discharge. The fact that the expansion was found to be 32% suggests that the cathode begun expanding before the zero porosity was reached. The end porosity, calculated from the above expansion figures, amounts to 0·11. It is interesting to note that the end porosity could not be reduced further by reducing the discharge rate.

Such high values of k_2 of 2·678 Ah g^{-1} were never achieved with low rate type (cylindrical) electrodes which, as a result of the cell design, were confined and had no room for expansion. The choking factor ϵ for those cathodes always remained below unity but the end porosity was similar to that of the high rate type (expanding) electrodes.

3.2. *Optimization of cell designs*

The cell design procedures are illustrated here for optimization of a cell that has to deliver 10 Ah at, say, a 0·4 A discharge rate. Table 1 shows the cell parameters in the order in which they were determined, some by calculations from the cell requirement data and some by an arbitrary selection. There are three distinguishable groups of parameters in Table 1. Listed in Group 1 are those

Table 1. Cell parameters: 10 Ah at 0·4 A

Group	*Parameter*	*Symbol*	*Value*
1	Weight of carbon	---	3·734 g
	Porosity of carbon	---	0·806
	Volume of carbon	---	9481 mm^3
	Cathode current density	---	1·25 mA cm^{-2}
	Surface area of cathode, both sides	---	$3{\cdot}2 \times 10^4$ mm^2
	Thickness of carbon	---	0·592 mm
	Equivalent thickness of screen	---	0·054 mm
2	Thickness of cathode	t_1	0·646 mm
	Width of cathode	H	45 mm
	Length of cathode	L_1	356·2 mm
	Volume of anode	V_a	6280 mm^3
	Diameter of mandril	D	12·6 mm
	Thickness of separators	t_2	0·25 mm
3	Thickness of all 4 components	t	1·507 mm
	Length of first separator	L_2	378·31 mm
	Length of anode	L_3	386·87 mm
	Length of second separator	L_4	399·22 mm
	Thickness of anode	t_3	0·361 mm
	Number of turns	n	5·45
	Internal diameter of can	D_c	28·34

calculated from the experimentally established characteristics of this type of carbon structure, leading to the calculations of the dimensions of the cathode. In Group 2 are the parameters that had to be determined before the final matching was made of the components of the electrode structure. The cathode width, H, and the separator thickness, t_2, were chosen arbitrarily. The first six parameters in Group 3 are the six unknowns in the system of six equations described in the theoretical part of this paper. These parameters were obtained in the computer program that used the parameters of Group 2 as its input data. The internal diameter of the can, D_c, was calculated last from the number of turns and the total thickness of all four components of the structure. A schematic presentation of a wound cell is shown in Fig. 4.

A somewhat more elaborate design procedure is followed when a cylindrical cell of fixed dimensions has to be optimized for discharge at a given rate. Such a case is illustrated next by optimizing the standard D, C and AA cells for discharge at 500, 200 and 75 mA, respectively, as shown in Table 2.

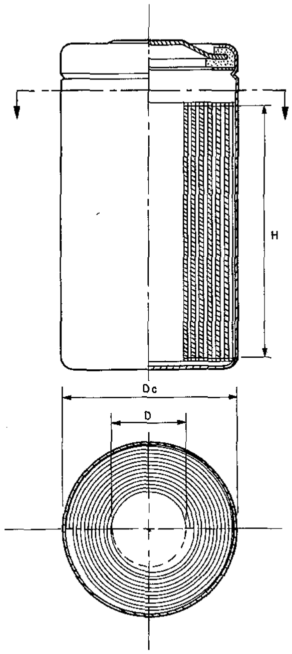

Fig. 4. Schematic presentation of a wound cell.

Group 1 of the parameters define the cell sizes and the discharge rates. The parameters in Group 2 are determined next. The usable space is determined by subtracting from the cell volume the

Table 2. Design parameters for standard size cells

Group		*Symbol*	*Dimension*	*Cell size*		
				(D)	(C)	(AA)
1	Outside dimensions					
	Diameter		cm	3·41	2·62	1·43
	Height		cm	6·11	4·92	5·0
	Maximum discharge current		mA	500	200	75
2	Usable space					
	Diameter	Dc	cm	3·05	2·30	1·20
	Height	H	cm	4·75	3·75	3·75
	Length of cathode	L_1	cm	41·66	21·05	7·89
	Thickness of cathode	t_2	cm	0·025	0·025	0·025
	Equivalent thickness, cathode screen	t_{cs}	cm	0·0051	0·0051	0·0051
	Equivalent thickness, anode screen	t_{as}	cm	0·0035	0·0035	0·0035
3	Length of first separator	L_2	cm	43·91	22·85	8·77
	Length of anode	L_3	cm	44·83	23·46	9·20
	Length of second separator	L_4	cm	45·76	24·07	9·64
	Thickness of cathode	t_1	cm	0·061	0·074	0·050
	Thickness of anode	t_3	cm	0·037	0·043	0·028
	Diameter of mandril	D	cm	1·39	1·09	0·55
	Number of turns	n	–	5·89	3·87	2·79
	Cell capacity	Q	Ah	11·62	5·74	1·40

space occupied by the components of the cell seal and the void space needed for the expansion of the electrodes and the electrolyte. The length of the cathode is determined from the maximum discharge current while the thickness of separator is chosen arbitrarily.

The parameters in Group 3 are all interdependent. Their values have to be determined in such a way that all cell components fit into a given cell space while the electrodes are matched both geometrically and electrochemically. They were determined by solving the following system of nine equations with nine unknowns, namely $n, L_2, L_3, L_4, t_1, t_3, D, Q$ and the total thickness, t, of anode, cathode and two separators:

$$L_1 = t\pi n^2 + D\pi n \qquad (28)$$

$$L_2 = L_1 + 2t_1\pi n \qquad (29)$$

$$L_3 = L_2 + 2t_2\pi n \qquad (30)$$

$$L_4 = L_3 + 2t_3\pi n \qquad (31)$$

$$t_1 = \frac{Q}{k_2 d_c L_1 H(1-P)} + t_{cs} \qquad (32)$$

$$t_3 = \frac{QME}{L_3 HFd_a} + t_{as} \qquad (33)$$

$$D = D_c - t(2n - 0{\cdot}5) \qquad (34)$$

$$Q = \frac{D^2\pi H}{4k_3} \qquad (35)$$

$$t = t_1 + 2t_2 + t_3. \qquad (36)$$

The values of the constants independent of cell size were:

$k_2 = 2{\cdot}678$ Ah g^{-1}

$d_c = 2{\cdot}03$ g cm^{-3}

$P = 0{\cdot}806$

$M = 6{\cdot}939$ g equiv.$^{-1}$

$E = 1{\cdot}25$

$d_a = 0{\cdot}534$ g cm^{-3}

$F = 26{\cdot}8$ Ah equiv.$^{-1}$

$k_3 = 0{\cdot}5643$ cm^3 Ah^{-1}

$t_{cs} = 0{\cdot}0051$ cm

$t_{as} = 0{\cdot}0035$ cm.

The equivalent thicknesses t_{cs} and t_{as} of the cathode and anode screen are the corresponding thicknesses of solid foils containing the same amount of metal per unit of the apparent surface area of the screen. The constants related to the cell size ($D_c H$, L_1 and t_2) are listed in Group 2 of Table 2 for each of the three cell sizes.

The following are the difficulties one could expect in building the cells to conform to the calculated parameters:

(1) The winding of the cell structure cannot easily be made so tight that there is no space left between different layers.

(2) Lithium foil is commercially available only in several standard thicknesses. Unless the plant is equipped to roll its own foil, the closest thickness will have to be selected from the list of available foils.

(3) The cathode thickness is variable within 0·05 and 0·2 cm, given the present state of the art, making designs with cathodes outside this range impractical.

(4) Tolerances in the thicknesses of electrodes and separators are within ±5% of the stated values.

(5) The separator material may not be capable of keeping the electrolyte within the electrodes at the end of discharge, when the electrolyte level in the centre of the roll begins to fall.

For these reasons one could expect somewhat lower cell discharge capacities than the values calculated for each three types of cells. Both the design and the craftsmanship could, therefore, be tested by determining the discrepancy between the calculated and the realized cell capacities.

Acknowledgment

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