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Materials balance in primary batteries. IV. Lithium batteries with organic electrolytes

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Part IV of the study of the materials balance in primary batteries concerns the application of the optimization procedure, developed for lithium inorganic batteries, to systems using organic electrolytes. The stoichiometric characteristics of discharge reactions (k_1 and k_3) were defined for six different lithium battery systems and the cathode discharge characteristics (k_2) were determined on the basis of the experimental data reported by various authors. These characteristics were then applied in the optimization procedure developed earlier to predict the maximum cell capacity obtainable at low discharge rates. The values predicted were compared with those reported by various authors; this suggests the magnitude of improvement possible with each of the systems if the present optimization procedure were applied. A good agreement was found between the predicted and the previously reported values for some systems (e.g. Li/CuO), while some other systems showed room for improvement. The optimization procedure was found inapplicable without modifications to one of the systems studied (Li/SO_2) due to the limitations in the volume available for the electrolyte.

1. Introduction

Discharge processes in primary batteries are accompanied by transformation of active materials into products of different physical characteristics, as well as a transfer of materials away from their primary sites within the electrode structure. Volume changes of active materials, for example, will always occur and have to be accommodated within the sealed cell with a minimal disturbance of the cell structure. A volume reduction on discharge within a rigid container results in the formation of gas bubbles that could inactivate sections of the electrode and thus reduce the cell discharge capacity.

A study was made of the influence of the volume reduction during discharge on the optimization procedures for lithium inorganic batteries [1]. It was shown that the cells made for low rate application must include an extra volume of electrolyte, stored outside the electrode structure to compensate for the volume reduction and avoid bubble formation within the electrode structure. These studies were extended to include the high rate cells made with wound electrodes [2]. A balance of all materials was considered for fresh and discharged cells. The specific cell capacity obtained per unit volume of discharge products (k_1, Ah cm^{-3}), the maximum specific capacity obtained per unit weight of carbon blend (k_2, Ah g^{-1}), and the specific volume reduction in the course of discharge (k_3, cm^3 Ah^{-1}) were the three parameters required to establish the relationship between electrical performance and the dimensional characteristics of the components within the fixed volume of a single cell. Tests conducted with these optimized cell structures, showed a considerable improvement in the cell discharge capacity. A method was described for solving the system of equations defining the dimensional characteristics of the electrode structure [3]. A computer programme was written and the data generated for the design of high power (wound) cells in three standard sizes and for cells of various rate capabilities made with various thicknesses of electrodes and separators.

The results of these studies could readily be applied in the design of other primary batteries. This work illustrates design procedures that should be followed in the optimization of lithium batteries involving organic electrolytes. Several systems, currently under development by various companies, are considered, with the emphasis on the problems in the design of cells for low rate discharge.

2. Stoichiometric characteristics of various systems

Six different lithium–organic electrolyte systems were included in the present study. Their cell discharge reactions are listed in Table 1 together with the values of the stoichiometric characteristics k_1 and k_3, calculated on the basis of their respective discharge reactions and the densities of the reactants and products involved.

The sulphur dioxide system has been described in more detail recently [4]. A lithium foil anode forms a galvanic couple with a porous carbon cathode in an electrolyte containing 70% liquid sulphur dioxide, the balance being a mix of acetonitrile and propylene carbonate, with 1.8 mol l^{-1} of LiBr dissolved in this liquid mixture. The open circuit voltage of these cells is 2.92 V at room temperature, showing a maximum at $-10°$C. Lithium dithionite is an insoluble discharge product precipitated within the pores of the carbon cathode during discharge. The active life of the cell is controlled by the cathode and is terminated when all the active cathode sites are blocked with discharge products. A significant volume reduction on discharge, predicted by these calculations, seems to be a dominating parameter in the design of an electrode structure that would be free of bubbles at the end of discharge.

The poly carbonmonofluoride system takes advantage of the capability of the graphite structure to bond fluorine in large quantities relative to the amount of graphite involved. Fluorine is available for discharge in a variety of electrolytes when this cathode material is combined with lithium anodes. The system has been described in detail [5–7] but with some disagreement as to the mechanism of the discharge reaction. The discharge proceeds with no net change in the quantity or the composition of the electrolyte. The conductivity of the electrolytes used in this and other systems described below, is significantly lower than that of the SO_2 electrolyte, thus limiting the rate capability of the cells made with these systems.

The remaining four systems listed in Table 1 have been described in more detail, as the research and development progressed [8–12]. Values of the stoichiometric characteristics, k_1 and k_3, will be combined with other characteristics of the systems in the calculations of the optimized cell structure in the remainder of this paper.

3. Cathode characteristics

Specific capacities, obtainable per unit weight of the cathode blend at low discharge rates, have been calculated based on the cathode compositions and their respective discharge reactions. These values (k_2, Ah g^{-1}) are listed in Table 2 along with the

Table 1. Stoichiometric characteristics of various battery systems using lithium anode in organic electrolytes

Battery system	*Cell discharge reaction*	*Capacity per unit volume of discharge products k_1 (Ah cm^{-3})*	*Specific volume reduction on discharge k_3 (cm^3 Ah^{-1})*
Li/SO_2	$2Li + 2SO_2 \rightarrow Li_2S_2O_4$	0·770	0·851
$Li/(CF)_n$	$(CF)_n + nLi \rightarrow C_n + nLiF$	1·769	0·337
Li/MoO_3	$2Li + MoO_3 \rightarrow Li_2O + MoO_2$	1·549	0·411
Li/V_2O_5	$2Li + V_2O_5 \rightarrow Li_2V_2O_5$	1·578	0·862
Li/CuO	$2Li + CuO \rightarrow Li_2O + Cu$	2·440	0·306
Li/Ag_2CrO_4	$2Li + Ag_2CrO_4 \rightarrow Li_2CrO_4 + 2Ag$	0·721	0·199

Table 2. Characteristics of cathodes used in various lithium–organic electrolyte battery systems

Battery system	*Cathode composition*	*Capacity per unit weight of cathode* k_2 *(Ah g⁻¹)*		*Optimum porosity*
		Theoretical	*Practical*	
Li/SO_2	80% Carbon black 20% Graphite		1·982 [4]	0·839
Li/$(CF)_n$	91% $(CF)_n$ 9% Graphite	0·786	0·682 [7]	0·504
Li/MoO_3	70% MoO_3 30% Graphite	0·260	0·208 [10]	0·347
Li/V_2O_5	70% V_2O_5 30% Graphite	0·206	0·217 [9]	0·294
Li/CuO	93.5% CuO 6.5% Graphite	0·635	0·580 [8]	0·594
Li/Ag_2CrO_4	70% Ag_2CrO_4 30% Graphite	0·113	0·089 [12]	0·419

practically obtained values, reported by various authors. With these values of k_2 it was possible to calculate the optimum porosity of dimensionally stable cathodes in the same way as reported earlier for the thionyl chloride system ([1] Equation 6):

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

for cathodes discharged at low rates ($\epsilon = 1$), with their respective starting densities d_c, g cm^{-3}. The porosity values obtained are also listed in Table 2.

The discharge mechanism of the lithium–sulphur dioxide system is, in many respects, similar to that involved in the lithium–thionyl chloride system. The electrodes are made in the same way with slight differences in the cathode structure and with different current collectors. A less efficient space utilization is expected in the sulphur dioxide system, however, due to the presence of the electrochemically inert inorganic solvants.

The maximum specific capacity obtained per unit weight of the carbon blend used (k_2, Ah g^{-1}) has been determined from the results reported by Bro *et al.* [4]. A typical cathode, measuring 165 mm x 38 mm x 0·9 mm with 80% porosity, delivered 3·9 Ah maximum. Such a cathode contained 2·013 g carbon, so that the value of k_2 was calculated to be 1·982 Ah g^{-1}. This value was obtained with a thin cathode used in making the high power type cells. It was used below to estimate the maximum cell capacity of the high energy type cells with the understanding that somewhat lower values of k_2 are obtained for the type of carbon blend used in building thick cylindrical cathodes.

The properties of fluorocarbon compounds have been studied by Watanabe *et al.* [5], while the electrochemical cells, based on fluorocarbon cathodes, have been introduced by Fukuda and Iijama [6]. Although the cell reaction mechanism is still being debated [11], there is no doubt about the identity of discharge products. The maximum specific capacity obtained per unit weight of the cathode blend (k_2, Ah g^{-1}) was estimated from the results obtained by Gunther [7] with flat thin electrodes. A cathode with 8.7% carbon in $(CF)_n$ delivered 1·48 Wh g^{-1} at an average discharge voltage of 2·17 V, resulting in the value of k_2 of 0·682 Ah g^{-1}.

Dampier [10] has reported an 80% utilization of MoO_3 in a cathode mixture containing 30% graphite. These data, combined with the discharge mechanism proposed (Table I), were sufficient to determine the value of k_2 (Ah g^{-1}) listed in Table 2 along with the optimum porosity calculated for this system under low rates of discharge.

Lang [9] has described in detail a cylindrical cell made with a V_2O_5 cathode. The discharge was reported for a very low rate, so that the maximum utilization of the active cathode material could be

Table 3. Maximum capacity of standard size cells made with various lithium–organic electrolyte systems

Battery system	*Specific capacity per unit volume of electrode structure (Ah cm^{-3})*	*Maximum capacity obtainable from standard size cylindrical cells (Ah)*		
		AA	C	D
Li/SO$_2$	0·332	1·651	5·629	12·676
Li/(CF)$_n$	0·484	2·408	8·206	18·480
Li/MoO$_3$	0·388	1·930	6·579	14·815
Li/V$_2$O$_5$	0·301	1·499	5·109	11·505
Li/CuO	0·769	3·825	13·039	29·362
Li/Ag$_2$CrO$_4$	2·62	1·303	4·442	10·002

assumed to have been achieved. The values of k_2 and the optimum porosity calculated are listed in Table 2.

Lehman *et al.* [8] have reported the data obtained with the standard size AA cell made with CuO cathode. With 6·5% graphite in the cathode [13] and the realized capacity of 3·83 Ah at low rates, the values of k_2 and the optimum porosity were calculated as listed in Table 2.

Lehman *et al.* [12] have also reported the performance of a standard size button cell (11·33 mm diameter x 5·20 mm high) made with the Ag$_2$CrO$_4$ cathode and discharged at extremely low rates. A claimed nominal capacity of 120 mAh (the realized capacity was somewhat lower) was used in calculating the values of k_2 and the optimum porosity listed in Table 2. These values are based on the two electron change discharge reaction only, as defined in Table 1.

4. Results and discussion

Based on the reaction mechanisms stated in Table 1 and on the discharge parameters for cathode materials stated in Table 2, it was possible to calculate the maximum capacity obtainable per unit volume of the electrode structure using the expression derived earlier ([1] Equation 13). These calculations have been carried out for all six electrochemical systems considered in this work. The results are shown in Table 3 along with the maximum capacity obtainable from the three standard sizes of cells, assuming they were all constructed with the electrodes arranged concentrically, with the lithium anode attached to the inside of the can wall and with a cylindrical cathode having a hole in the centre equal in volume to the total volume reduction on discharge. The useful volume, available for placement of the electrode structure in each of the three cell sizes, has been established on the basis of experience with crimped cell closures. The values used earlier in the design of the wound cells were smaller for practical reasons, since the entire electrode package had to be preassembled outside the can and then placed into the can, the internal diameter of which was reduced by the depth of the groove supporting the seal components. The electrodes in the low rate (concentric) structure can be formed inside the can, utilizing the entire internal diameter of the can. The maximum values of the volume of the electrode structure were used in the calculation of the data presented in Table 3. They were 4·975, 16·956 and 38·182 cm^3 for the AA, C and D cells, respectively. A brief comment is offered here regarding the comparison of the calculated data in Table 3 with the reported data, on which the calculation is based.

A significant improvement is possible in the deliverable capacity of the Li/SO$_2$ system in cells designed for low discharge rates. Achieving the same specific cathode capacity as that with thin electrodes at higher rates (k_2, 1·982 Ah g^{-1}) should not be difficult, if the rate of discharge is significantly reduced. The present procedure is based on the assumption that an excess of the electrolyte is automatically ensured, when the electrodes are optimized with the porous cathode being the capacity controlling factor. This assumption must be valid (at sufficiently low rates) for all organic electrolyte systems that do not consume the electrolyte in the course of discharge. Only

Table 4. Maximum energy densities obtainable with various lithium–organic electrolyte systems

Battery system	*Operating voltage (V)*	*Weight reference*	*Energy density*	
			(Wh dm^{-3})	*(Wh kg^{-1})*
Li/SO_2	2·80	[4]	635	362
Li/$(CF)_n$	2·75	[14]	909	497
Li/MoO_3	2·80	est	742	312
Li/V_2O_5	2·65	[9]	569	221
Li/CuO	1·3	est	683	292
Li/Ag_2CrO_4	3·03	est	542	214

one of the systems considered in this paper does not fall into this category, namely, the Li/SO_2 system. It was necessary, therefore to establish the minimum volume of the electrolyte required to support the predicted cell capacity and compare it with the values experienced in practice. The standard size Li/SO_2 C cell, for example, would require 15·36 ml electrolyte at 100% SO_2 utilization to deliver the predicted capacity of 5·629 Ah but in practice, one was never able to pack in more than 13 ml. For this reason the optimization procedures for the Li/SO_2 cells have to be modified and a somewhat lower maximum capacity will result.

Some increase in the maximum cell capacity is possible with Li/$(CF)_n$ cells as well. A capacity of 6·3 Ah has been claimed for the Matsushita C size cell, [14], while the calculations (Table 3) predict a maximum of 8·2 Ah. There was no information available on the performances of the Li/MoO_3, Li/V_2O_5 or Li/Ag_2CrO_4 systems in standard size cells, so it was not possible to estimate the differences between the actual cell capacities and the values predicted for the optimized electrode structures. The predicted performance for the Li/Ag_2CrO_4 system does not appear spectacular if one assumes only a two electron change in the discharge reaction. However, a deeper discharge has been indicated for these cathodes [13], and this increases significantly the maximum capacity obtainable from the standard size cells, but reliable data are not available.

An interesting example of the performance of an optimized cell construction has emerged from the design calculations for the Li/CuO system. The performance of the AA size cell reported [8, 13] seems to indicate the most efficient use of the space available in the standard AA cell with which the discharge data were obtained. The agreement between the predicted (3·825 Ah) and realized (3·830 Ah) capacity for the AA cell is remarkable. There seems to be no way of improving further the capacity of this cell.

The maximum volumetric energy densities realizable with each of the six electrochemical systems have been calculated using the data reported for the operating voltage at low discharge rates, the predicted cell capacity and the overall volume of the standard size cells. The gravimetric energy densities were calculated for those systems for which the weights of the finished standard cells were reported, and estimated for those systems for which the weight data were not available. The energy densities are shown in Table 4. The comparison of the maximum energy densities obtainable with each of the six systems serves not only as a guide in selecting the system to be used for a particular application, but also as a measure of achievement in the development efforts indicated by the ratio of the predicted and realized performance data.

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