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## Lithium - Thionyl Chloride Battery State-of-the-Art Assessment

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## **Lithium - Thionyl Chloride Battery State-of-the-Art Assessment**

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### **Abstract**

Models of the performance of primary Li/SOCl<sub>2</sub> cells can provide for realistic comparisons between technical information from different sources, and set standards that electronic circuit designers may refer to in the generation of high-quality products. Data from various investigators were used to derive mathematical - statistical relationships with physical design features (e.g. size and materials), operating parameters (e.g. current and temperature) and storage conditions (time and temperature). These efforts were substantially promoted by normalization procedures. For example, current loads were converted into current densities, or if appropriate, into current per unit cathode volume. Similarly, cell capacities were standardized with the maximum values observed at low current and also with respect to the cathode volume. Particular emphasis was placed on evaluations of voltage-delay, cell capacity and self-discharge, for which several equations were established.

In spite of a considerable expenditure in time to find high-quality datasets, the reality is that all of the reviewed studies are flawed in one way or another. Specifically, all datasets are afflicted with sizable experimental errors and the precision of the regression equations is much lower than is deemed necessary for a universal model of the lithium thionyl chloride cell. Each of the equations has some definite truth content, but is generally incapable of bridging the gap between different studies.

The basic failure to come up with a unifying model for Li/SOCl<sub>2</sub> batteries leaves only one benefit of the present analysis, namely to provide guidance for future investigations. Several recommendations are made based on the insight gained during the search for good data in the relevant literature.

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# **Lithium - Thionyl Chloride Battery**

## **State-of-the-Art Assessment**

### **Introduction**

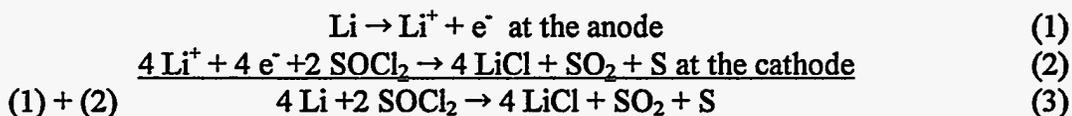
Nearly thirty years of research on lithium primary batteries have produced a wealth of information, which, however, is difficult to comprehend in its details and specific relevance. Although the Li - thionyl chloride system yields high open circuit voltage and energy density, it has start-up problems after storage (i.e. voltage-delay), shows diminished capacity at low temperature, self - discharges at elevated temperature, and presents an explosion hazards under high-load conditions. While remedies for all of these problems have been found over the years, there often remain questions as to what trade-off a specific remedy may require, if applied to a particular cell design. For example, an additive in the electrolyte that minimizes voltage-delay may increase the self-discharge. Or, a special cathode composition for improved low temperature performance may destabilize the cell at elevated temperature.

This report describes efforts toward the development of a mathematical-statistical model that unifies, as much as possible, the seemingly divergent pieces of information contained in the scientific literature. Such a model, in its final form, would have great analytical and predictive value for users as well as for researchers of Li/SOCl<sub>2</sub> batteries. There are, however, a few obstacles, which must be overcome before this goal can be realistically achieved. For instance, it requires fundamental insight and technical expertise to benefit from published data in the modeling effort, because authors of technical disclosures usually provide processed, not raw data, and limit themselves to the essentials of their investigations while omitting proprietary details. At the other extreme are publications that proliferate in information of questionable value. One difficulty with the use of data from published sources has to do with the variety of test vehicles in different studies, which can only be overcome by appropriate normalization.

The organization of this report reflects the progress made to date in the modeling effort. Operating principles for Li/SOCl<sub>2</sub> cells are first discussed to provide the context for expected correlations. Next, options for empirical curve fitting methods are discussed to justify the approach taken in the data analyses that follow. Results from selected datasets on voltage-delay, cell capacity and self - discharge, which were successfully modeled with mathematical-statistical formulas, are presented and discussed together with other data that were found to be less well suited for incorporation in the model. The variables that yielded quantitative correlations with the experimental responses are (1) operating temperature, (2) current load, (3) storage time, (4) storage temperature and (5) carbon type. Achieving consistency between different datasets is the primary goal, that in some aspects remains elusive and may require specifically targeted new evaluations.

## Operating Principles for Li/SOCl<sub>2</sub> Cells

Li/SOCl<sub>2</sub> cells have anodes of lithium foil laminated to a nickel grid, cathodes of polytetrafluoro ethylene (PTFE) -bonded porous carbon, also on a nickel grid, a separator between the electrodes and a solution of LiAlCl<sub>4</sub> in thionyl chloride as electrolyte. The electrode reactions are:



Lithium in contact with thionyl chloride instantaneously corrodes according to equation (3) to form a passivating layer of insoluble LiCl. Investigators perceive this passivation layer as a crucially important inhibitor that precludes continued direct reaction of lithium with thionyl chloride, but does not render the cell nonfunctional. As a result, there should always be some small residual level of reactivity that is called 'self - discharge.' The LiCl layer builds up with time and can block current flow on discharge, which then gives rise to 'voltage delay.' Continued current flow depassivates the anode surface and leads, after interruption of the current, to a very high rate of self - discharge that subsides only as the LiCl layer reforms over days or weeks.

During normal cell discharge, LiCl precipitates not at the anode surface but in the pores of the carbon cathode. Since the carbon surface catalyzes the electron transfer to the thionyl chloride, filling the pores in the carbon composite with LiCl has the result of progressively deactivating the cathode. If the current distribution in the porous cathode is uniform, then the LiCl precipitation is uniform throughout the volume. This is the case at low current levels, while at higher currents the pores near the aggregate surface become more strongly polarized and, therefore, receive a proportionately larger amount of the precipitate. Eventually, not only the LiCl-filled pores at the outer surface, but also the open pores in the center layers of the cathode become electrochemically inaccessible and the electrode reaction stops prematurely.

By design, Li/SOCl<sub>2</sub> cells are cathode-limited for the following reason. A cell in series with other cells, if depleted of all anode material, may become polarized to a degree that finely divided lithium particles electrodeposit in the cathode pores. Reaction (3) can then initiate a thermal runaway situation and lead to rapid venting of the cell. The excess amount of lithium must be adjusted for the self - discharge over extended storage times, and there must be a reserve of thionyl chloride as well.

As seen from the above discussions, the capacity of a Li/SOCl<sub>2</sub> cell is primarily determined by the mass, the pore volume and the catalytic efficiency of the cathode and also depends on the temperature and the discharge rate. Because of the latter, it seems appropriate to normalize the discharge current with respect to the cathode volume (dimension A/cm<sup>3</sup>), instead of referring the current to the cathode area (dimension A/cm<sup>2</sup>). The design of a low-rate cell incorporates relatively thick electrodes with small area. Since

the discharge current is low, the cathode pores will be uniformly accessible, thus preserving the cell capacity. Simultaneously, the self - discharge remains minimal, since reaction (3) is proportional to the lithium surface area. High-rate cells require more electrode area, and the cathode accessibility at high currents must be enhanced by decreasing the carbon layer thickness to shorten the diffusion path. More separator material and more electrolyte are needed, and the self - discharge rate unavoidably increases in this case.

## Options for Nonlinear Statistical Models

The basic modeling philosophy for the task at hand focused on the available information about thionyl chloride batteries. Apart from general principles, such as, for example, proportionality between self - discharge and lithium area, there are no known mathematical functions that describe the system. Frequently, the operating parameters such as test temperature, storage temperature and storage time produce nonlinear responses, which can be reasonably fitted with polynomial regression. However, extrapolation of polynomials to conditions outside the tested range may produce absurd values. Certain characteristics of the data suggest ways for their correct analysis, as follows:

1. Cell capacity and voltage-delay can approach zero, but never assume negative values. At zero, the variance is also zero.
2. Cell capacity never exceeds some maximum value that is only observable at low current and moderate temperature. At this capacity the variance is likely to be smaller than at intermediate values.
3. Voltage delay (as measured by the time required for the voltage to recover after starting the current flow) seems to rapidly rise, after the control variables exceed certain threshold values. The standard deviation is likely to be proportional to the magnitude of the voltage-delay.

This suggests that the voltage-delay be modeled with a logarithmic function, while some sigmoid function is appropriate for the cell capacity.

Unfortunately, investigators usually report very short voltage-delays as zero, which is unacceptable for the logarithmic fit as it biases the error structure. This problem was resolved with a compromise, where 0's were replaced with values halfway between 0 and the next smallest number in the data set.

Selim and Bro<sup>1</sup> proposed the following hyperbolic tangent function as a model for the capacity - rate correlation of primary batteries in general:

$$C / C_o = \tanh ((i/R)^{1/A}) / (i/R)^{1/A} \quad (4)$$

where  $i$  = battery current,

$C, C_o$  = realized and maximum battery capacities,

$A, R$  = empirical parameters that control the shape and the location of the S-curve.

This function is depicted in Figure 1 for selected values of the two empirical parameters. An isosbestic point occurs at  $(R, 0.76)$ , while the inflection points of a family of curves fall on a line through ordinate 0.565 at abscissa values that increase with  $A$ . The S-shape is asymmetric, with the slope changing faster before than after the inflection point. This feature is illustrated in Figure 1 by means of (absolute values) of the second derivative, showing that the curvature to the left of the inflection point is greater than that to the right. Contrary to this characteristic, actual capacity curves for  $\text{Li}/\text{SOCl}_2$  cells seem to be steepest as they approach zero. Alternatives to the hyperbolic tangent function were therefore evaluated.

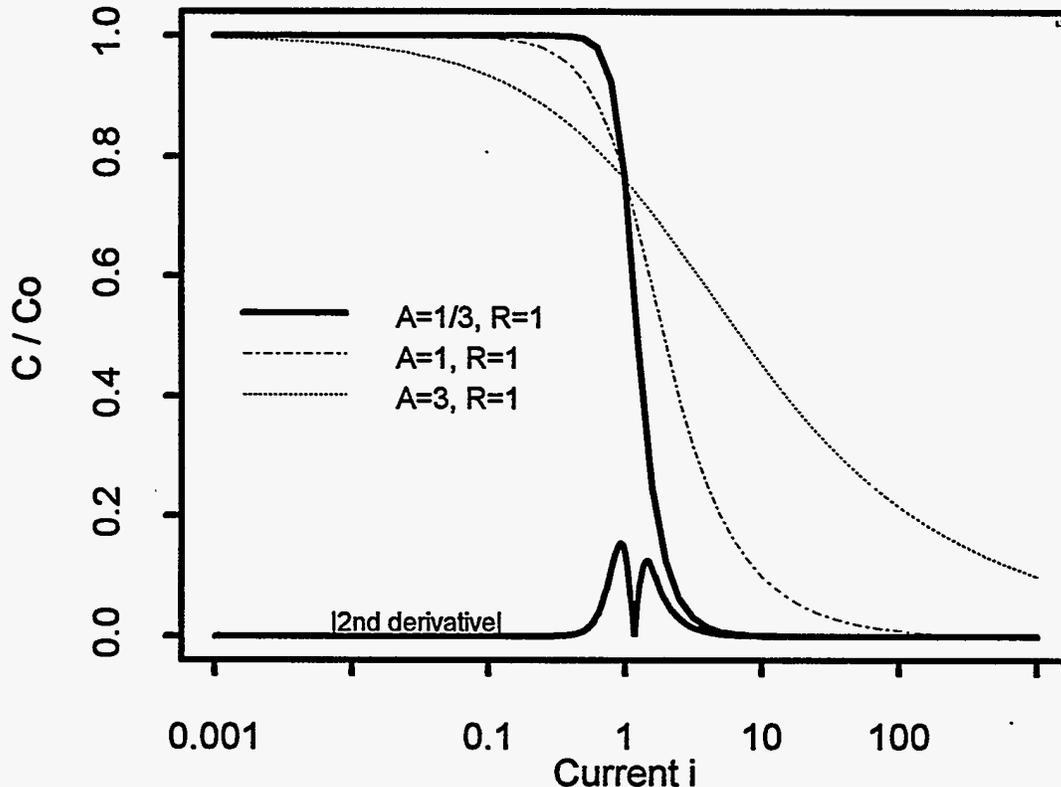


Figure 1: Features of the hyperbolic tangent function for modeling cell capacity.

Among numerous choices<sup>2</sup> to more closely match the shapes of modeled and experimental curves the Weibull function was found to be most satisfactory:

$$C / C_o = \exp(-(i/b)^a) \quad (5)$$

where  $i$  = battery current,

$C, C_o$  = realized and maximum battery capacities,

$a, b$  = empirical parameters referred to as shape factor and location factor.

For Weibull functions, the inflection points and the isosbestic point are identical at  $(b, 0.368)$ , and the S-shape is asymmetric, as desired, with the slope changing slower before than after the inflection point, as shown in Figure 2. Both features, the lower lying

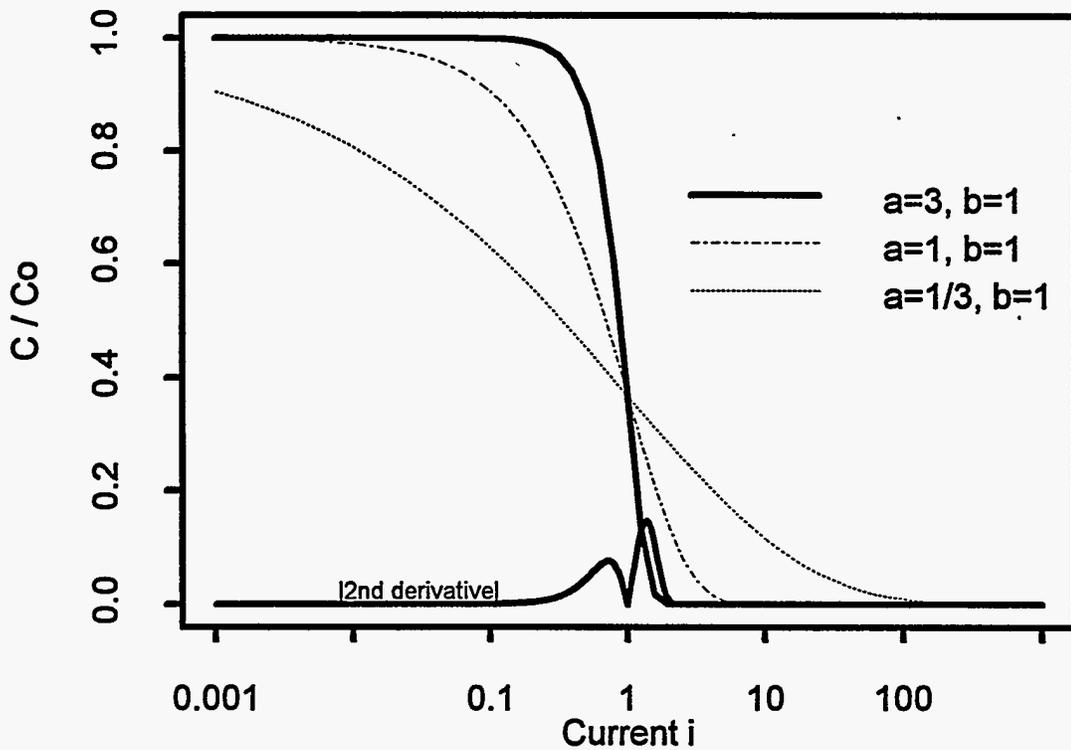


Figure 2: Features of the Weibull function for modeling cell capacity.

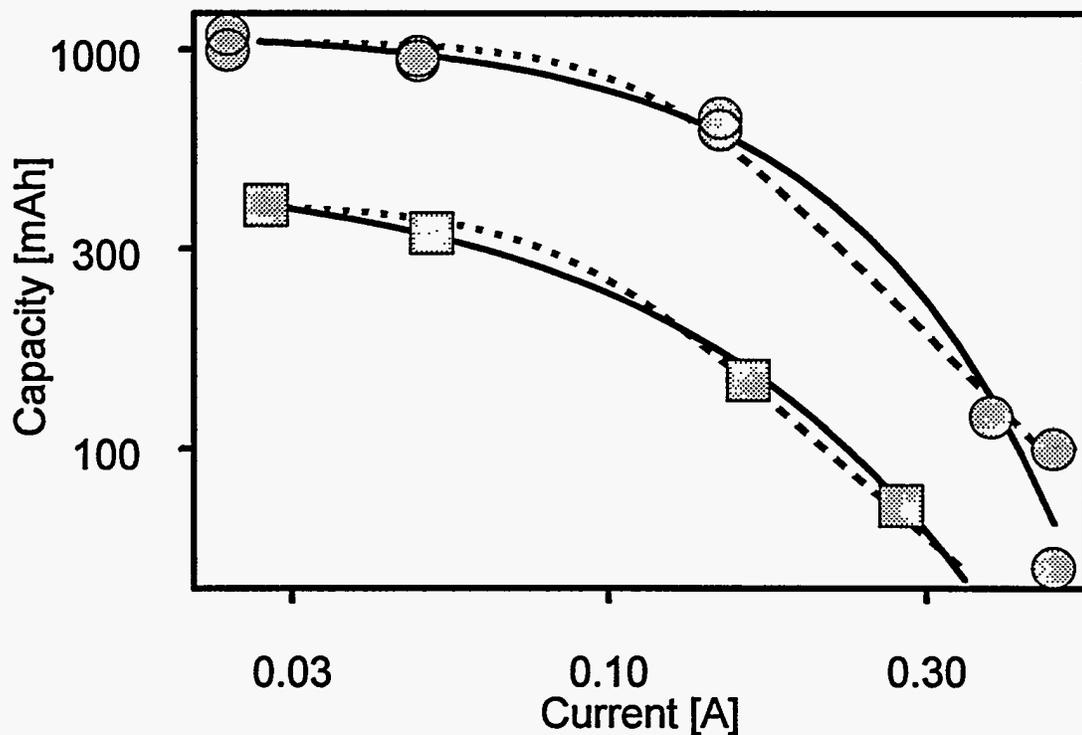


Figure 3: Selim and Bro's data (circles) fitted with the hyperbolic (dashed line) and the Weibull functions. Also, some other experimental data (squares), arbitrarily scaled to fit the coordinate range.

inflection point and the modified curvature lead to more reasonable fitting characteristics, although there is no theoretical reason to favor either of these empirical functions. As illustrated in Figure 3, the hyperbolic tangent function yields a plateau when the experimental data already show a downward trend.

One practical disadvantage of the hyperbolic tangent function is that its inverse function is undefined. However, the Weibull function equation (5) can be rewritten as

$$\ln(-\ln(C / C_0)) = a \ln(i) - a \ln(b) \quad (6)$$

which shows that a linear least squares fit of the transformed experimental data versus the control variables yields the parameters  $a$  and  $b$ . Zero - capacity readings must be excluded from the datasets, and there is a possibility that the double logarithmic transformation creates some bias in the error structure.

### **Datasets on Voltage-Delay**

Recent publications on voltage-delay emphasize the hypothesized correlation with the complex impedance of the passivation layer, but, unfortunately, fail to demonstrate the causative effect of the passivation layer<sup>3</sup>. One paper by Morrison and Marincic<sup>4</sup> addresses the dependence of the cell voltage on (1) storage temperature, (2) storage time, (3) number of current pulses (of 0.3 Asec) and (4) electrolyte concentration, presumably in support of the claim that tetrachlorogallate provides for better performance than tetrachloroaluminate. Although this paper presents a total of 107 data points for  $\text{LiAlCl}_4$  electrolytes, only 24 measurements were made after the longer storage time of 11.6 days, which makes this an unbalanced experimental design. In addition, the use of current pulses of 2 seconds duration precludes the detection of short voltage-delays. These circumstances of the experimental design have the effect that almost no information can be extracted from the data, and a least squares analysis only explains about 20 % of the total variance, and no further information is provided on random or systematic error sources. The authors claim (without proof) that voltage-delay, and particularly the "early failure problem" of cells stored above 70 C, is caused by the deposition of aluminum on the lithium surface, where an inert alloy is supposed to form that inhibits the anode reaction. Reportedly,  $\text{LiGaCl}_4$  electrolyte does not deposit gallium and effectively prevents voltage-delay.

Earlier studies on voltage-delay reflect a more direct approach to investigating the problem, by taking measurements of the time required for the voltage to return to some acceptable level after a load is applied. Ohsaki<sup>5</sup> reports on the effects of eight polymers on voltage-delay and suggests that chlorine-substituted additives are the most potent agents for preventing voltage-delay. The polymer additions were studied in combination with storage times of 20 and 40 days at 60 C and 6 months at 20 C, respectively, yielding 24 variable combinations. Each of the test conditions was replicated 3 - 6 times, but only averages are reported. The observed delay times, measured at a current density of about 8

mA/cm<sup>2</sup>, range from 0 to about 850 seconds. Ohsaki's results were subjected to an analysis of variance, using a logarithmic transformation for which the single zero in the dataset was replaced with 0.2. About 80 % of the total variance can be assigned to the additives, while 10 % are caused by the storage conditions. This result implies high quality of the data, particularly in view of the random character of the polymer variable. An attempt to further evaluate the effects of the storage conditions by regression was hampered by Ohsaki's selection of levels for storage time and temperature, which are poorly balanced. In a simple least squares analysis the coefficients of these two variables are not different from zero. However, if the storage times,  $t_s$ , are multiplied with the respective (absolute) storage temperatures,  $T_s$ , a modified variable is obtained with the dimension Kdays.  $T_s t_s$  can be viewed as a thermal energy-time integral that yields a very satisfactory fit of the data. For the complete regression, the symbol A and numbers 1 to 9 were assigned to the different additives. The numbers stand for: 1) Rubber chloride, 2) Chlorinated polyethylene, 3) No additive, 4) Chlorinated polypropylene, 5) Polyethylene, 6) Polyvinylidene chloride, 7) Chlorinated polyvinyl chloride, 8) Polyvinyl chloride and 9) Vinyl chloride - vinylidene chloride copolymer. The following equation explains 92% of the total observed variance ( F-statistics: 92.4 on 4 and 20 degrees of freedom):

$$\log_{10}(V_{\text{delay}} [\text{sec}]) = 2.73 - 1.51 \cdot 10^{-5} T_s t_s - 0.0242 A^2 - 1.39 \cdot 10^{-6} A^7 + 1.634 \cdot 10^{-8} A^9 \pm 0.324 \quad (7)$$

Unfortunately, the  $T_s t_s$  dependence is counterintuitive, as it suggests increased voltage-delay for decreasing temperature - time products, i.e. for fresh cells. Figure 4 illustrates the fit that equation (7) provides.

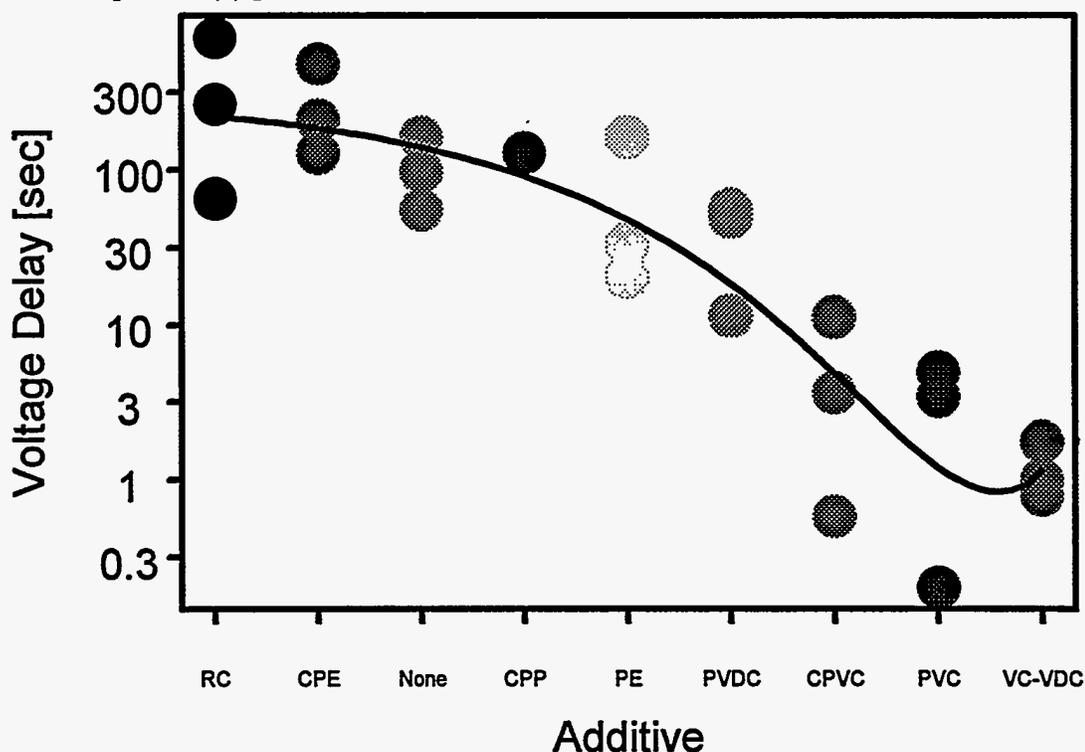


Figure 4: The effect of additives on the voltage-delay, with a regression line added according to equation (7) for  $T_s t_s = 24240$  Kdays.

Another dataset on voltage-delay is available from a 1976 report by Dey<sup>6</sup>, with measurements (in seconds) ranging from zero to infinity. In order to enable a logarithmic transformation, zeros were replaced with 0.1 and infinities with 10,000 seconds. The independent variables in this study were:

1. Cell current, converted for the present analysis by division with the lithium area to current densities (I): 0.65, 2.6 and 7.8 mA/cm<sup>2</sup>.
2. Storage temperature (T<sub>s</sub>): 328 and 345 K (55 and 72 C).
3. Storage duration (t<sub>s</sub>) at 55 C: 14, 28, 84 and 180 days; at 72 C: 7, 14, 28 and 90 days.
4. Test temperature (T<sub>t</sub>): -30 and 25 C.

One data point is missing in an otherwise balanced experimental design. An analysis of variance suggested that about 74 % of the total variance can be explained in terms of linear and quadratic effects and interactions of the current density, the storage time and the storage temperature, but there is no significant effect of the test temperature. A regression analysis led to the following equation, which accounts for almost 76 % of the total variance (F-statistics: 25.6 on 5 and 41 degrees of freedom):

$$\begin{aligned} \log_{10}(V_{\text{delay}} [\text{sec}]) = & 3.236 - 2.073/I \\ & - 0.506 t_s + 0.000119 t_s^2 \\ & + 0.00147 t_s T_s + 0.0141 T_s/I \pm 0.709 \end{aligned} \quad (8)$$

The standard error shown in this equation surpasses that of equation (7), but the sign of the term in equation (8) is in line with expectations. Figure 5 shows Dey's data plotted against the storage time, with regression lines for the three current densities, as calculated from equation (8). Obviously, higher current, higher temperature and longer storage time all cause the voltage-delay to increase, but the large amount of scattering dampens the confidence in the regression lines.

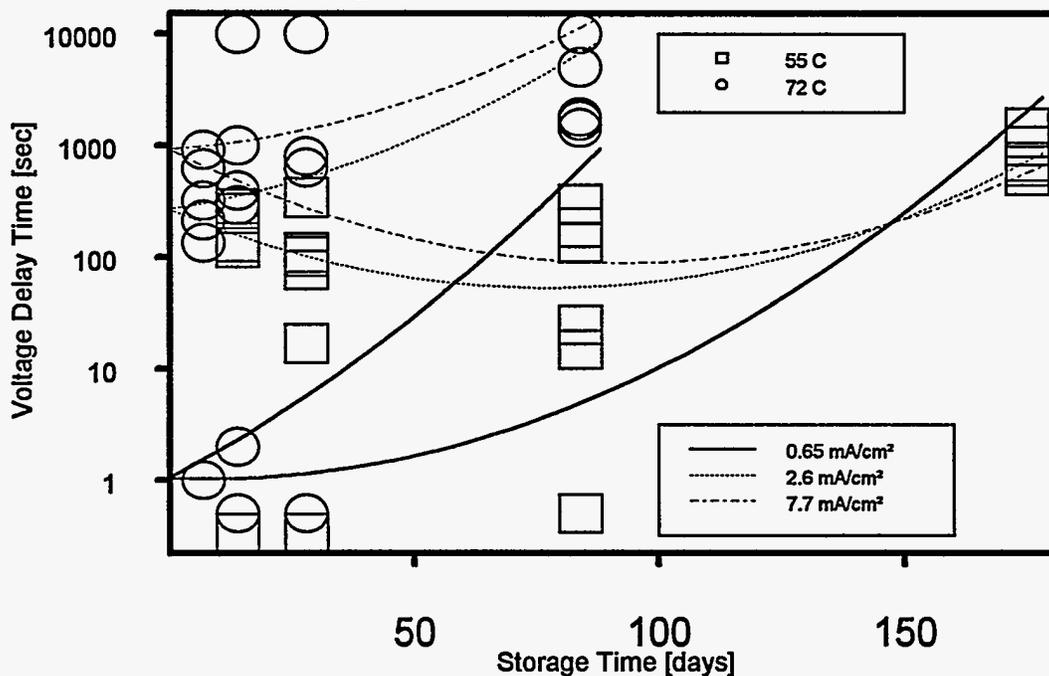


Figure 5: Dey's data on voltage-delay, with regression lines according to equation 8.

## Data Sets on Cell Capacity

The above referenced paper by Dey also includes data on cell capacity, measured for the same variable combinations as for the voltage-delay tests and using a 2 Volt endpoint standard. Various attempts to find a polynomial fit of the data were successful only in the statistical sense that a high percentage of the total observed variance could be explained by the variables. However, the shapes of the fitted lines outside the boundaries of the test variables were inconsistent with the experimental trends of the responses, and clearly unsuitable for extrapolations. For this reason, the data were fitted to the Weibull function by way of equation (6), which required substitution of all zero capacities with a value  $>0$ . Also, the raw data needed to be normalized with a capacity that is slightly greater than the observed maximum capacity. Choosing 0.01 Ah and 12.6 Ah, respectively, did not bias the error structure in any significant way.

The dataset contains 56 measurements. Since the cell capacity is cathode - limited, the cell currents as well as the responses were normalized with the cathode volume ( $9.36 \text{ cm}^3$ ). Using variable identifications as for equation (8), where  $I$  is now in  $\text{A/cm}^3$ , the following equation was obtained by multivariate regression:

$$C[\text{Ah/cm}^3] = 12.6 \exp(-\exp(0.452 \ln(I) - 0.168 t_s - 0.0371 / t_s - 8.99 \cdot 10^{-5} T_t T_s + 2.903 \cdot 10^{-9} T_t t_s^3 + 5.12 \cdot 10^{-4} T_s t_s + 0.520 \pm 0.283)) \quad (9)$$

This equation accounts for 92 % of the total observed variance (F-statistics: 94.9 on 6 and 49 degrees of freedom). Figure 6a shows the normal probability plot of the residuals of the regression and confirms, by the reasonably straight-lined arrangement of the points, that the transformation introduced no undue bias. After back - transforming the data, the distribution becomes slightly skewed, as illustrated in Figure 6b.

These results may be compared with data collected on fresh cells at Sandia National Laboratories in the 1993/94 time frame. Six temperatures (-55, -40, -18, 25, 50 and 70 C) and four resistance loads (10, 50, 250 and 400 Ohms) were combined in 23 out of the 24 possible combinations. There are numerous replications for some variable combinations (e.g. 14 for 25 C and 50 Ohms), but others only have 3, for a total of 145 measurements. The group variances are inhomogeneous, with 6 of the 23 variances outside the 95% homoscedasticity range, which suggests that the cells had manufacturing flaws, or came from different sources, or were mishandled during the tests. A regression analysis analogous to the one used for Dey's data yielded a fit that explains about 60 % of the total variance. For a comparison with this earlier dataset, a contourplot was generated from the raw data after normalization with the cathode volume, Figure 7. Overlaid are contourlines obtained with equation (9) by setting  $T_s$  to 345 K (72 C) and  $t_s$  to 100 days, for a reasonable lineup with the Sandia data. This comparison shows that Dey's cells after high temperature storage perform as well as Sandia's fresh cells. Since the cells have cathode - limited capacity, the reason for the difference should be sought in the cathode material.

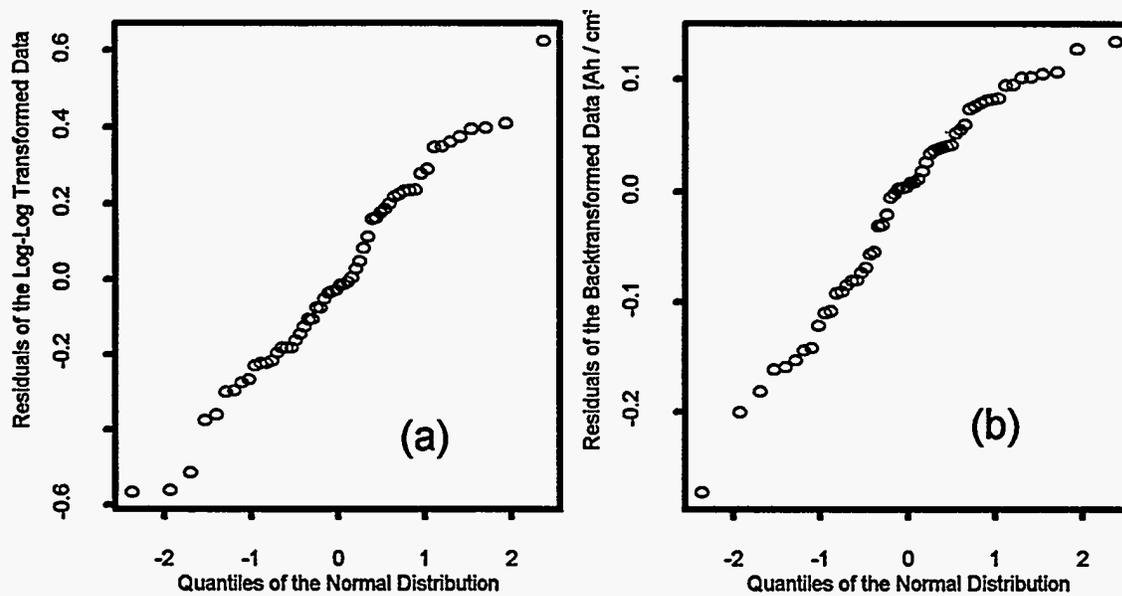


Figure 6: Residuals from the regression analysis showing close to normal distributions.

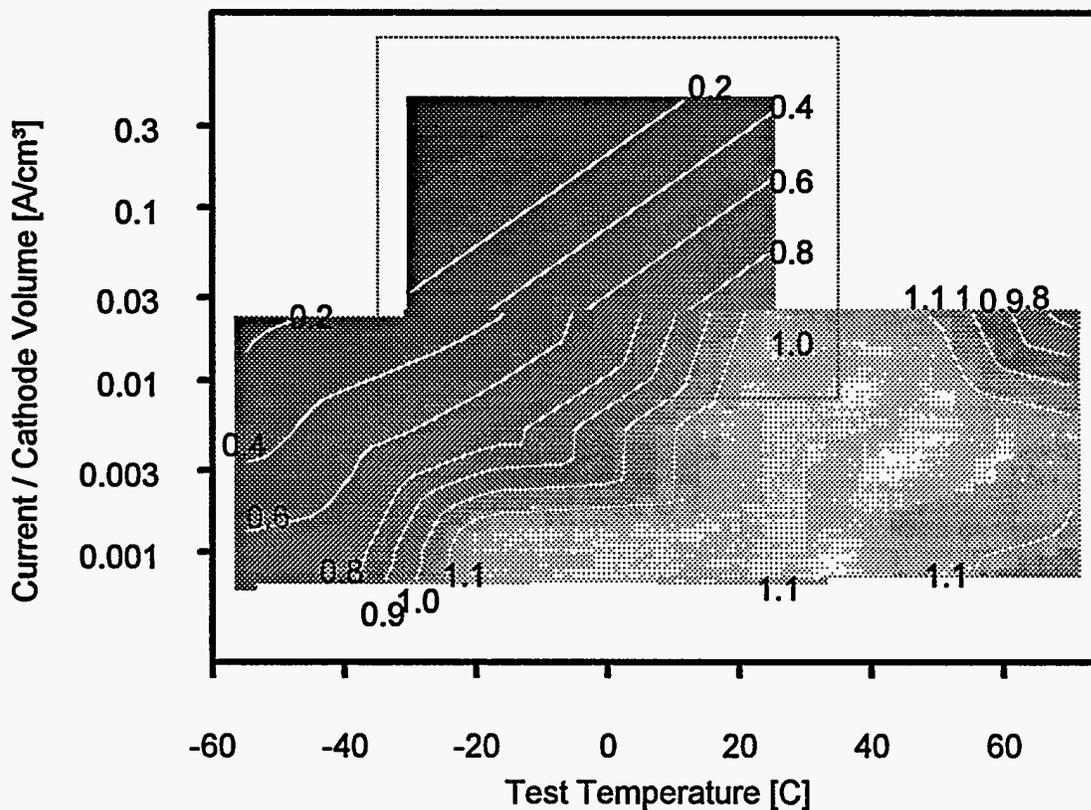


Figure 7: Contour plot of cell capacities in  $\text{Ah}/\text{cm}^3$ . Sandia data are in lower rectangle, while contour lines from equation (9) with  $T_s = 345 \text{ K}$  and  $t_s = 100 \text{ days}$  are in framed area.

In another publication, Dey<sup>7</sup> demonstrated the effect of carbon on the performance of 63 Li/SOCl<sub>2</sub> cells. Twelve types of carbon were used to prepare cathodes with either 170 or 226 cm<sup>2</sup> area, of somewhat variable thickness and carbon content. The discharge current ranged from 0.03 to 3 A per cell, but not all cells were treated equally. Dey provides information on the carbon types in terms of trade names and various physical properties, of which only the apparent density proved to influence the cell capacity. Some crucial information is missing, e.g., no cathode thickness is given for one of two batches of cells made with Shawinigan Black (they were assumed to be equal). For graphite cathodes the thickness is also missing, but could be estimated from the weight and the density.

Analogous to the additives in the Ohsaki dataset, "carbon type" is a random variable, which, for the numerical representation in a mathematical model, requires the assignment of arbitrary numbers to the carbon types. The statistical fitting procedure benefits from ranking the responses in terms of their maximum capacity and from the normalization of the cell capacities with the cathode volume. Figure 8 shows that most of the carbons fall into a rather broad range of capacities between 0.7 and 1.1 Ah/cm<sup>3</sup>, while two groups behave distinctly different. The high-performing cells are made with Shawinigan Black, and achieve capacities two times higher than the next best performer. By contrast, cells made with graphite lag far behind the performance of the median cell, particularly as the load increases. For a comparison of these responses with Dey's earlier dataset, equation 9 was used (with T<sub>i</sub> = 25 C, T<sub>s</sub> = 328 K and t<sub>s</sub> = 1 hour) to insert the labeled line.

Further normalization of the data with each carbon type's maximum capacity, C<sub>o</sub>, (as measured or interpolated at low load), removes most but far from all of the divergence. A polynomial regression produced the following equation:

$$C / C_o = \exp(-\exp(0.452 \ln(I) + 1.295 d_{carb}^2 + 0.00589 / d_{carb}^2 - 0.552 x + 0.00135 x^4 - 8.632 \cdot 10^{-8} x^8 \pm 1.1334)) \quad (10)$$

where, d<sub>carb</sub> in g/cm<sup>3</sup> stands for the apparent density of the raw carbon, and x ranges from 1 to 12, for the different carbon types. Equation (10) accounts for about 53 % of the variance (F-statistics 9.14 on 6 and 48 degrees of freedom). Although the quality of this fit is relatively poor on account of the numerical representation of the carbon type, it features a coefficient for the ln(I) factor (i.e. the shape factor a of the Weibull function) that exactly matches the one in equation (9), and therefore raises the confidence in this correlation. Having the carbon density included in equation (10) as a significant contributor to the cell capacity attests to the importance of the cathode preparation (Note: lower density yields higher capacity).

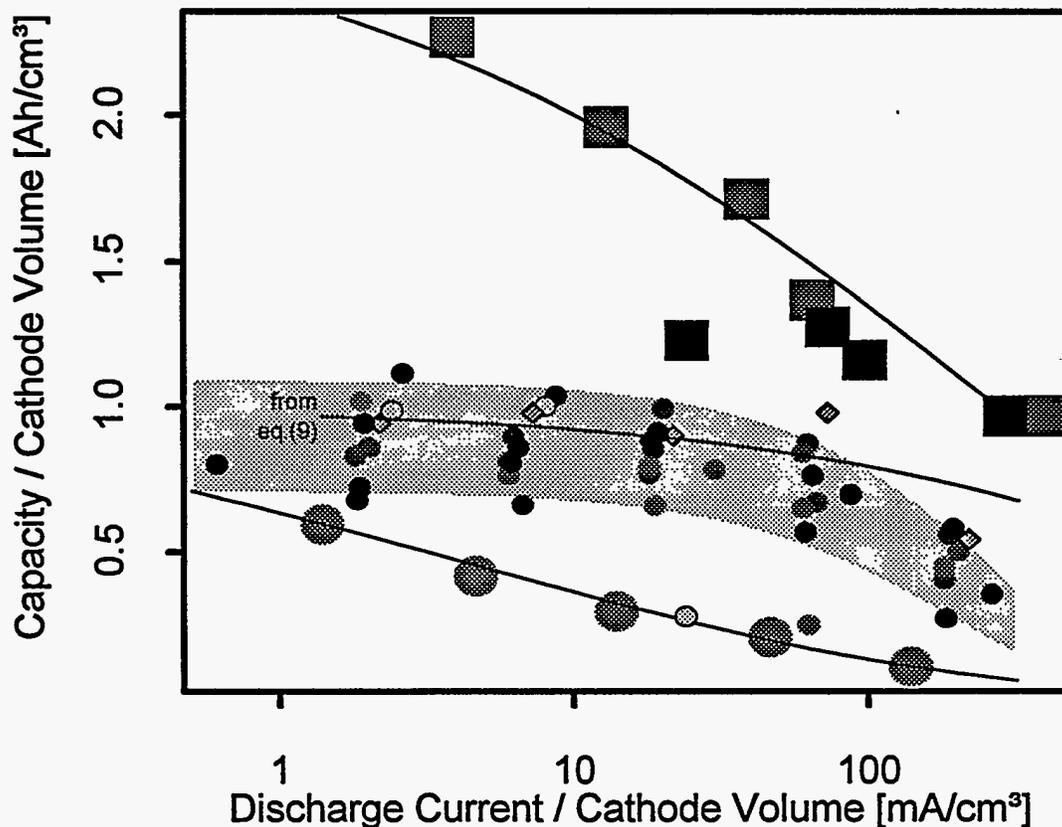


Figure 8: Variation of cell capacity with discharge current and carbon type. Ten of the twelve carbon types fall in the shaded regime, while Shawinigan Black greatly outperforms all other carbons. Graphite performs poorly, as expected.

### Datasets on Self - Discharge

Information on the self - discharge of Li / SOCl<sub>2</sub> cells has been published by several investigators, notably by Hansen and Frank<sup>8</sup> and by Takeuchi, Meyer and Holmes.<sup>9</sup> These papers describe microcalorimetric tests and already provide equations that relate the self - discharge to either the time at open circuit, or the depth of discharge. Hansen and Frank's data were collected at 25 and 65 C, using cells with a capacity of 0.28 Ah. No anode area is specified, but their results in terms of power ( $q$  in  $\mu$ W) per cell can be summarized by combining the authors' two equations into one:

$$q = \exp(27.855 - 0.0475 T - 3.0638 \ln(t) - 0.0076 T \ln(t)) \quad (11)$$

where  $T$  is temperature in K and  $t$  is time since activation of the cell in seconds. Integration over the 2 years' testing period yields capacity losses of 0.177 Ah (63%) at 65 C and 0.023 Ah (4.4%) at 25 C, respectively.

Takeuchi et al. tested 2.8 Ah cells with 14.5 cm<sup>2</sup> anode surface at 37 C, and applied current densities of 25, 12, 5 and 2.5 μA/cm<sup>2</sup>. Over periods of up to 7 years the ratio of lost-to-delivered capacity ranged from 0.66 (at 25 μA/cm<sup>2</sup>) to 0.17 (at 5 μA/cm<sup>2</sup>).

The applicability of this information to average use conditions is uncertain, at present, because the method of collecting the data probably underestimates the self-discharge rate. A study, which is now in progress at SNL, determined that temperature variations can disrupt the integrity of the LiCl film and depassivate the cell. Accordingly, a well-thermostated cell, e.g. one in a microcalorimeter, will achieve a more perfect passivation layer and show less self-discharge than a cell that experiences temperature fluctuations in normal use or storage. There is also evidence that pulsed current significantly aggravates the self-discharge over the rate typical for DC loads of comparable discharge rate. A report on these findings will be issued soon.<sup>10</sup>

## Summary and Conclusion

Models of the performance of primary Li/SOCl<sub>2</sub> cells can provide for realistic comparisons between technical information from different sources, and set standards that electronic circuit designers may refer to in the generation of high-quality products. Data from various investigators were used to derive mathematical-statistical relationships with physical design features (e.g. size and materials), operating parameters (e.g. current and temperature) and storage conditions (time and temperature). These efforts were substantially promoted by normalization procedures. For example, current loads were converted into current densities, or if appropriate, into current per unit cathode volume. Similarly, cell capacities were standardized with the maximum values observed at low current and also with respect to the cathode volume. Particular emphasis was placed on evaluations of voltage-delay, cell capacity and self-discharge, for which several equations (7 through 11) were established.

In spite of a considerable expenditure in time to find high-quality datasets, the reality is that all of the reviewed studies are flawed in one way or another. Specifically, all datasets are afflicted with sizable experimental errors and the precision of the regression equations is much lower than is deemed necessary for a universal model of the lithium thionyl chloride cell. Each of the equations has some definite truth content, but is generally incapable of bridging the gap between different studies. For example, equation (7) clearly demonstrates the efficacy of various additives to reduce voltage-delay, but is clearly flawed with respect to the effects of storage time and temperature. Equation (8) seems to reasonably correlate voltage-delay with current density and storage time at elevated temperature. However, the dataset contains an excessive amount of unexplained variability, and, being limited to two storage temperatures, any extrapolations to other storage conditions, e.g. room temperature, are unreliable. The agreement between these two equations is rather inadequate. Similar problems exist with equations (9) and (10), which suggest strong effects of temperature and cathode composition on the cell capacity. However, they provide no clue whether or not a specially designed cathode could

compensate for the capacity loss that is typical for low temperature operation. Finally, equation (11) on self-discharge is based on data which were collected under stable temperature conditions, when in fact there is mounting evidence that the dynamics of temperature fluctuations control the self-discharge of Li/SOCl<sub>2</sub> cells. This raises the possibility of the referenced experimental work being not more than an academic exercise.

The basic failure to come up with a unifying model for Li/SOCl<sub>2</sub> batteries leaves only one benefit of the present analysis, namely to provide guidance for future investigations. The following recommendations are based on the insight gained during the search for good data in the relevant literature:

1. It is highly unlikely, though not entirely impossible, that important publications on the Li/SOCl<sub>2</sub> system were missed, and that adequate reconciliation between the datasets in question can be achieved. Therefore, any plans for further evaluations of published datasets require a careful cost-benefit analysis.
2. New investigations should give high priority to analyzing the faradaic efficiency of Li/SOCl<sub>2</sub> cells, particularly for intermediate and low discharge rates. Such a study is now in progress,<sup>10</sup> but additional work will be needed to address the capacity shortfalls that this work implies.
3. Although methods for reducing voltage-delay have been developed, there is essentially no information available on how these schemes affect the self-discharge of the cells. For example, if additives of the type described in reference (5) have significant detrimental effects on the cell capacity, it would be unreasonable to use them.
4. The cell capacity of cathode-limited systems strongly depends on factors such as current load, operating temperature, aging conditions and carbon type in the cathode. Very little is known about the interactions between these factors, whereas a unifying model of the Li/SOCl<sub>2</sub> system seems unworkable without them. Since synergisms between load conditions and carbon type, and between aging characteristics and operating temperature are most likely, the study of these variable combinations seems to offer the greatest pay-back.

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