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Capacity Loss and Faradaic Efficiency of Lithium Thionyl Chloride Cells

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Abstract

In lithium / thionyl chloride (Li/TC) cells, a lithium limited design was thought to be safer than a cathode limited design because the amount of lithium left in discharged cells would be minimal. However, lithium corrosion reduces the capacity faster than does cathode degradation during storage. The optimization of the ratio of lithium to carbon was studied, considering storage time and temperature. The efficiency of converting chemical energy into electrical energy has been studied for the case of D cells with surface area from 45 to 345 cm^2, under constant and various pulsed loads. Microcalorimetric monitoring of the heat output during discharge allowed the direct measurement of the faradaic efficiency, and showed that self-discharge is far more pervasive than previously acknowledged.[1] Typical faradaic efficiencies for constant load varied from 30% at low current density to 90% at moderate and 75% at high current density. Pulsed current further depresses these efficiencies, except at very low average current density.

Introduction

The purpose of this work was to determine guidelines for the optimal construction of Li/TC cells according to the expected storage time and current density of the applications. In order to obtain the best materials balance for the highest energy density, a determination of the rate of degradation of real capacity caused by lithium corrosion and by cathode degradation is needed. The optimum balance would depend upon storage conditions. The assumptions are made that lithium corrosion reduces the available thionyl chloride, but that cathode deterioration does not.

Cell Capacity

Concentrically constructed, hermetic C size cells, 1" O.D. x 2" long, were used as test vehicles to determine capacity loss as a function of storage time at ambient temperature and at 60°C. Cells all containing identical 1-g cathodes, and 1.5 M $LiAlCl_4$ were built with a series of five different anode thickness (9, 14, 18, 21, & 26 mil). After the cells were stored at ambient or 60°C, they were discharged at ambient temperature with 34 or 100 ohm loads. For lithium limited cells, the difference between the observed capacity and the expected capacity reflected the amount lithium loss to corrosion.

The result of lithium capacity loss as a function of storage time is shown in Figure 1. The rate of loss due to lithium corrosion decreases with time, as observed by other researchers.[2] Lithium loss during storage at ambient temperature was not as rapid as it was at 60°C. At 60°C, the rate of loss was about 4.4 μA/cm^2 and decreased slightly after 140 days to about 2.3μA/cm^2.

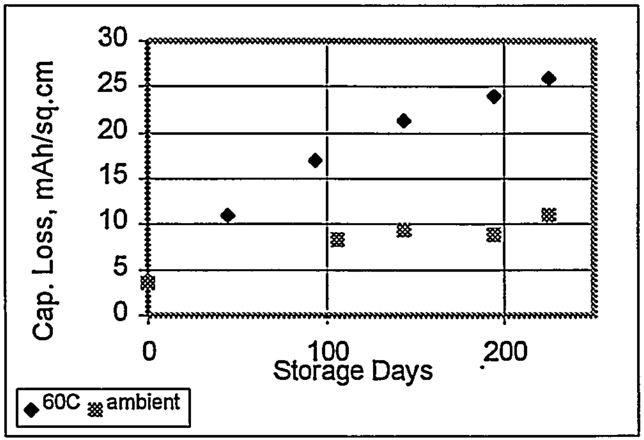

Figure 1 Lithium capacity loss for anode limited C cells.

The capacity of cathode limited cells as a function of storage time is shown in Figure 2. The capacity varied between 3.5 and 5.5 Ah/g of carbon at 1 mA/ cm^2 on a 0.06" cathode. This high capacity could be attributed to the elasticity of the cathode and the availability of volume for expansion in the cells. The data beyond 200 days were collected from cells which originally had 26-mil lithium.

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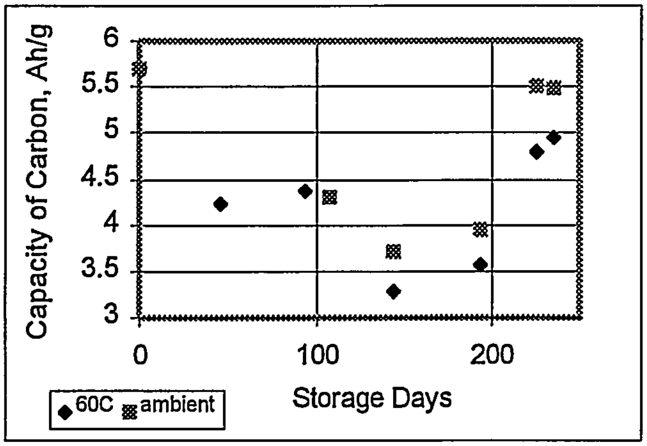

Figure 2 Carbon capacity for cathode limited C cells.

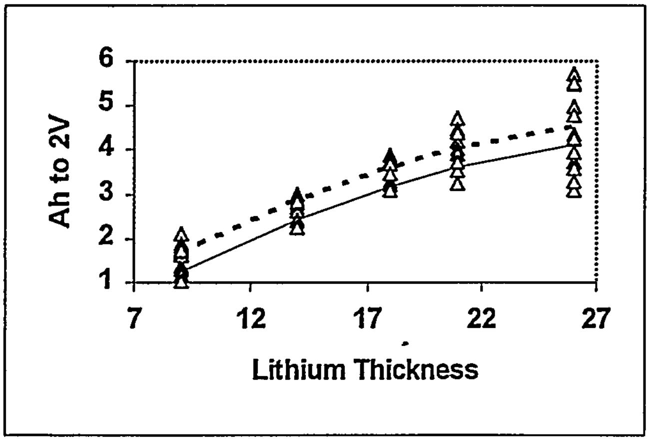

Figure 3 Capacity discharged at constant resistance load of 100 ohm at ambient after aging at ambient or 60°C up to 225 days. Lines are statistical fits for cells aged at 225 days at 60°C (solid) and at ambient (dotted).

Figure 3 presents the discharged cell capacity as a function of lithium thickness, discharge load, storage temperature and time. A statistical analysis of the result is shown in Table I. The adjusted R^2 was 86.4% and the p-value of the store-day was 0.083. The misfit was mainly caused by the data from the truly cathode limited cells stored longer than 200 days. However, dependent variables such as lithium thickness, 1/T, and discharge load were consistent as shown by the very small p-values. No other work we could find had evaluated truly cathode limited cells. In some work, cells would start as cathode limited, but after storage, the lithium was corroded away and the cells became lithium limited. [1a] Figure 3 shows that the cells are cathode limited when the initial lithium thickness is greater is than 21-mil. At 235 days and 60°C, the loss of lithium is about one Ah per cell. Cathode capacity is conventionally estimated assuming 2.0 to 3.5 Ah per gram of carbon. Considering storage time (235 days) and temperature (60°C), an additional one Ah of lithium is needed for this cell design. We plan to continue the experiment for another 12 months to observe the behavior of these cells.

Effects of Direct and Pulsed Current on the Self-Discharge

Self-discharge of Li/TC cells comes about because of the direct reaction of lithium with the solvent, according to

$$4\,\mathrm{Li} + 2\,\mathrm{SOCl_2} \rightarrow 4\,\mathrm{LiCl} + \mathrm{SO_2} + \mathrm{S} \qquad (1)$$

Useful energy can only be extracted by means of the two separate reactions

$$\mathrm{Li} \rightarrow \mathrm{Li^+} + e^- \text{ at the anode} \qquad (2)$$

and

$$4\,\mathrm{Li^+} + 4\,e^- + 2\mathrm{SOCl_2} \rightarrow 4\,\mathrm{LiCl} + \mathrm{SO_2} + \mathrm{S}$$

at the cathode. (3)

Accumulating LiCl at the lithium-electrolyte interface slows reaction (1) and has been referred to as a passivation layer or solid electrolyte interface, SEI.[3] The SEI presumably is a pure ion conductor that blocks all charge transfer reactions, but allows Li^+ ions to freely migrate from the lithium metal surface into the liquid electrolyte.

Passage of current enhances the self-discharge of Li/TC cells, apparently because the passivation layer breaks down and allows thionyl chloride to directly react with the lithium anode according to reaction 1. If reactions 1 and 2 proceed completely independent of each other, then any current-induced exposure of lithium metal will bring about a proportional increase of the self-discharge rate and lead to a faradaic efficiency of less than 1. In the absence of such a surface-cleaning current, the cell will still self-discharge in proportion to the area of lithium that is not protected by the lithium chloride layer. Averaged over time, this translates into reduced faradaic efficiency.

Some applications call for uninterrupted use of Li/TC cells, while others require pulse conditions where a comparatively long off period follows a short period of high current. The latter conditions were expected to present the worst possible situation, but as Figure 4 shows, the lowest faradaic efficiency is associated with the lowest average current density. The data in Figure 4 are all based on microcalorimetric determinations of the heat flow from Li/TC cells during constant discharge and pulsed discharge loads. Because of the slow rate at which cells approach steady state conditions, each test was run for a minimum of 3 hours. D cells with surface area from 45 to 345 cm^2 were used in a Hart Model 1701 Microcalorimeter. Apart from controlling the on-off duty cycle and the pulse height of the discharge current, two temperatures, 5 and 30°C, were selected for evaluation, as were cells with different anode areas and different electrolyte concentrations. Using current densities, in lieu of current, eliminates cell size as

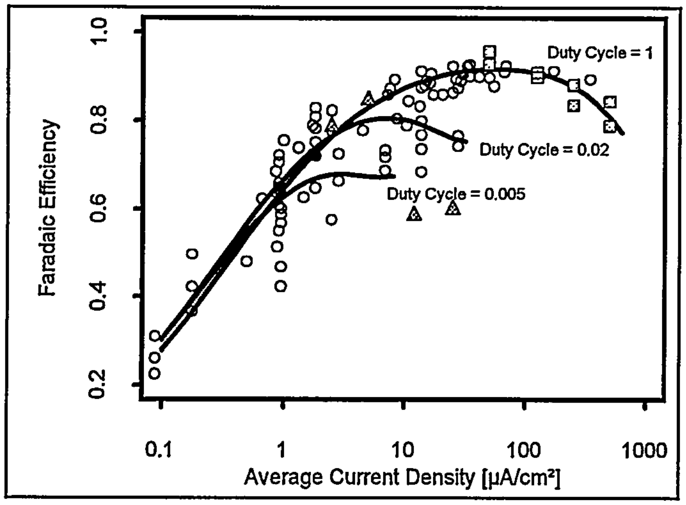

Figure 4 Effect of current density and duty cycle on the faradaic efficiency of Li/TC cells. Squares and triangles refer to constant discharge data from references 4 and 5, respectively.

a factor, but the differences in electrolyte concentration were ignored in the data analysis. Overall, the experiment design is somewhat unbalanced, because it is not practical to test numerous cells with well defined depths of discharge Expenditures in time and material would have been prohibitive. The slow rate of data acquisition of the microcalorimeter necessitated that each cell be tested under numerous current loads, in order to save time on equipment equilibration. Therefore, if there is an effect of the prior history of a cell it will not be recognized, but the experimental error will be increased. Eight points in Figure 4 (square symbols) come from P. Bro's paper[4] and four more from that of Takeuchi et al.[5] (triangles). They refer to constant current and were measured at 25 and 45°C.

The calculation of faradaic efficiencies from microcalorimetric measurements has been discussed in the literature, e.g. by Takeuchi et al.,[5] and involves the separation of several contributions to the total heat output of the cell. In our studies, the cell was placed in the cavity of the calorimeter and connected via thin wires to either a precision resistor (for constant discharge tests) or to an electronic power supply (for pulse measurements). Therefore, all energy from the cell, which could be put to some useful purpose, dissipates outside the calorimeter. Energy dissipation inside the cell derives from three processes, (1) heat due to an IR drop across the internal cell resistance, (2) entropic heat associated with the anode and cathode reactions, i. e. the Peltier effect, and (3) heat from the self-discharge reaction. Item (1) is small and can be neglected, unless the internal resistance is high at very low temperature or has risen to several Ohms as the result of a deep discharge. The entropic heat follows from thermodynamic data for reaction (1)[6,7] and corresponds to about 0.43 T mV (41.3 T Wsec/F), where T is the absolute temperature. Referring this value to the open circuit voltage of 3.65 V yields the ideal heat evolution in the cell as a fraction of the useful energy (3.6% at 30 C). Therefore, if Q_{sd} is the heat due to self-discharge, Q_c the calorimetrically measured heat and Q_e the externally dissipated energy, it follows that

$$Q_{sd} = Q_c - 0.43\,T\,Q_e \qquad (4)$$

and the faradaic efficiency becomes

$$E_{farad} = 1 - Q_{sd} / Q_e \qquad (5)$$

The faradaic efficiency data shown in Figure 4 were subjected to a statistical regression analysis with temperature T_c [C] , current pulse height I_p [μA/cm^2], duty cycle P, and average current density J [μA/cm^2] as independent variables. Since efficiencies only vary between zero and one, it is necessary to transform the raw data in order to achieve homogeneity of the system variance. Choosing the Weibull function as a model[8] requires that the regression be carried out consistent with the equation

$$\log(-\log(1-E_{farad})) = f(T, I_p, P, \log(J)) \qquad (6)$$

Table II shows that the variables log(J) and I_p plus four interactions yield a reasonably good fit to the data, including those taken from Bro's paper. The regression lines shown in Figure 4 were calculated with the coefficients of Table II, for 30°C and for three levels of the duty cycle P. As seen in the graph, the effect of P disappears as the current density decreases below 1 μA/cm^2. With regard to the effect of temperature, although the interactions between temperature and duty cycle are statistically significant, the practical impact of temperature is not very large.

Summary and Conclusion

The optimal design for Li/TC cells to be used within 200 days has been shown to be a 21-mil thickness of lithium with 4.7 Ah and a 60-mil thickness of carbon weighing one gram. The efficiency of converting chemical energy into electrical energy has been studied for low and medium rate lithium/ thionyl chloride cells, under constant and various pulsed loads. Microcalorimetric monitoring of the heat output during discharge allowed the direct measurement of the faradaic efficiency, and showed that self-discharge is far more pervasive than previously acknowledged by researchers and battery manufacturers.

Acknowledgments

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Table I: Multiple Regression Analysis of capacity data:
Capacity=f(Li thickness, storetemp, storedays, discharge load)
Residual Standard Error = 0.029, Multiple R-Square = 0.864
N = 58, F-statistic = 74.4 on 5 and 53 df, p-Value = 0

	Coefficient	Standard Error	t-Statistic	p-Value
Intercept	-6.084	1.2596	-4.830	0.000
Li thickness,mil	0.367	0.0603	6.085	0.000
Storetemp, 1000/°K	1.232	0.3279	3.759	0.000
Li Thickness ^{2}	-0.006	0.0017	-3.339	0.002
discharge load, ohm	0.011	0.0032	3.457	0.001
storeday	-.001	0.0008	-1.768	0.083

Table II: Multiple Regression Analysis of Faradaic Efficiency Data on a transformed scale according to equation (6)
Residual Standard Error = 0.1485, Multiple R-Square = 0.92
N = 90, F-statistic = 121.8 on 8 and 81 df, p-Value = 0

	Coefficient	Standard Error	t Statistic	p.Value
Intercept	0.1529	0.0366	4.1743	0.0001
I_p	$-8.777\ 10^{-4}$	0.0002	-5.6226	0.0000
log(J)	1.2482	0.0892	13.9955	0.0000
P	--0.6850	0.1548	-4.4248	0.0000
$\log(J)^2$	-0.2312	0.0174	-13.3230	0.0000
$T_c \times \log(J)$	-0.0106	0.0023	-4.5874	0.0000
$T_c \times I_p^2$	$1.126\ 10^{-8}$	0.0000	4.1889	0.0001
$T_c \times I_p^3$	$-1.260\ 10^{-12}$	0.0000	-3.6576	0.0005
$T_c \times P^3$	0.0189	0.0043	4.3855	0.0000

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