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DEVELOPMENT OF A MODERATE RATE LITHIUM/THIONYL-CHLORIDE "D" CELL

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Abstract

We have designed a lithium/thionyl chloride "D" cell for efficient performance at the moderate rate of ~ 500 mA (6.25 Ω load). The SNL-MR-D cell has 345 cm^2 of active electrode area, 1.0 M $LiAlCl_4$ electrolyte that may have SO_2 additive, and a cathode blended of Shawinigan Acetylene Black, Cabot Black Pearls 2000, and Teflon binder. The average performance of cells built in-house and discharged at 25°C and 6.25 Ω has been 14.9 Ah (50 Wh). We have aged the cells at 30°C and 50°C, and measured complex impedance and microcalorimetry during the aging period. The cells have been discharged after the aging period at 25°C and 0°C. This preliminary study has allowed us to establish an initial cell design and estimate the rate of capacity loss on storage or long-term usage.

Introduction

We design cells for specific applications that generally require high reliability and long shelf lives. For a $Li/SOCl_2$ "D" cell, one need is for a cell that can efficiently perform at very low rates for up to 10 years and also perform well under a 6.25 Ω load (500 - 550 mA). In this instance, the temperature range is relatively benign: 0 to 30°C. In order to make the cell an attractive alternative to Li/SO_2, it must possess substantially higher energy density in a safe package. We designed our cell based on some of the available literature that was applicable to our needs.

Dey and Bro looked at electrode geometry as a function of rate[1]. They showed that a 0.030" thick cathode would efficiently accomodate discharge products at moderate rates (<2 mA/cm^2). Data in this and another work[2] show that 1.0 M $LiAlCl_4/SOCl_2$ electrolyte gives the best energy density at these rates. In addition, it has been indicated that higher concentrations of $LiAlCl_4$ cause increased corrosion and passivation of the Li[3]. Based on these data, we chose a 0.030" thick cathode and 345 cm^2 of active surface area in our spiral-wound D cell. The cell is not wound tightly, so that space is available for cathode expansion on discharge[4-6]. We use a 1.0 M electrolyte, with the addition of SO_2 as a voltage delay additive[7] in some of our tests.

This design, at the 500 mA rate, is capacity-limited by blockage of the carbon cathode matrix. Klinedinst's work has indicated that the high surface area carbons (particularly Ketjenblack EC and Cabot Black Pearls 2000) discharge more efficiently than Shawinigan Acetylene Black, at least at high rates[8]. Therefore, we looked at cathodes, all with 8% TFE binder, made of only Shawinigan (SAB), and made of equal by weight blends of Ketjenblack KJ/SAB or Black Pearls BP/SAB. We also had a requirement for low self-discharge which, of course, was greatly affected by the choice of carbon. Early on in our study we discarded the Ketjenblack blended cathode because it aged very poorly, as Klinedinst and Harris later showed[9]. Their work, consistent with ours, showed that the BP/SAB blend gave the best capacity retention and least voltage delay after accelerated aging studies.

The need for a mechanical vent to release pressure to prevent explosion of $Li/SOCl_2$ cells is widely acknowledged[10-13]. Dey first explored the idea of vent pressures less than 200 psi[10], and his work was supported by Staniewicz et al[11]. While higher pressures may be safe for cells of a particular design[12,13], we selected the lower pressure as the conservative choice for our design.

Experimental

All tests were conducted in our "D" cell hardware. The cans are 304L stainless steel into which a 316L stainless steel burst disc (BS&B Safety Systems) has been laser-welded. All metal hardware, including the Ni electrode screens, is degreased and oven dried. We laminate Li foil to the anode screens by hand. The cathodes are formed from a dough which is rolled and pressed onto the screens. Both electrodes are 1.78" wide. They are weighed and measured prior to final assembly, both for quality control and for later performance analysis. We use an unbonded glass separator product, Whatman DBS30. The separator is 2" wide.

We purchase Lithco electrolyte, and then reflux it in the presence of Li. The SO_2 is added to complex with the $LiAlCl_4$ after the reflux operation. Cells are evacuated, filled and ball-sealed in an argon-atmosphere glove box, using a back pressure of 9 psi argon to deliver the electrolyte.

The cell has excess $SOCl_2$ capacity equalling 1.2X that of the Li. The balance is as follows: 19.3 Ah theoretical of electrolyte, 16.1 Ah theoretical of Li, and 14 Ah empirical of carbon at a 500 mA design rate. As noted above, the cell has 345 cm^2 of active electrode surface area.

Results

Safety and Abuse Tests

Short circuit tests at ambient temperature (3 replicates) produced maximum currents of close to 30 amps and cell skin temperatures of ~100°C. The vents opened fully after 3-5 minutes and allowed some expulsion of cell materials, but no noticeable flame. Short circuit tests at 70°C (4 replicates) caused similar ventings in less than 4 minutes, maximum currents of about 25 amps, and peak temperatures of 90 -103°C.

High rate 3.0A constant current discharge and reversal tests at 70°C (6 replicates) produced venting at skin temperatures of 85-125°C, within 100 minutes of entering reversal. Cell materials were partially expelled, but there was very little liquid and no smoke or flame in any of the tests.

High rate 3.0A charge tests at 70°C (6 replicates) produced benign, flameless ventings at 100 - 120 °C. When a test was continued beyond venting, it would eventually cause a higher temperature excursion and flame.

Our standard 6.25 Ω resistive discharge has never caused any bulging, leaking or venting in more than 80 tests.

Discharge Performance

Three variations in cell design were studied: 1) BP/SAB blended cathode with 1.0 M $LiAlCl_4/SOCl_2$ electrolyte (BP on Figures), 2) BP/SAB blended cathode with 1.0 M $LiAlCl_4/SOCl_2 \cdot SO_2$ electrolyte (BP & SO_2) and 3) SAB cathode with 1.0 M $LiAlCl_4/SOCl_2$ electrolyte (SAB).

Cells have been stored at 30°C and 50°C for times of 5 to 30 weeks, and tests to 120 weeks are still running. We have stored cells at open circuit and under low drain (150 µA). A cell is discharged following the aging period under a 6.25 Ω load at 25°C or 0°C. There were 2 or 3 replicates scheduled per condition.

Figures 1 through 3 show typical discharge performance for cells at 25°C. The fresh cells, Figure 1, run longer and at higher voltage with BP in the cathode. After aging at 30°C, Figure 2, the SAB cathode shows substantial voltage delay. BP in the cathode greatly improves the voltage response, and SO_2 makes a smaller positive improvement. These effects are more pronounced after aging at 50°C, Figure 3. In general, the BP cathodes greatly improve capacity, decrease self-discharge, and reduce voltage delay over the standard SAB cathodes. The effect of the SO_2 additive, while minor for this discharge condition, does reproducibly increase the average discharge voltage of the aged BP cathode cells.

Similar data for 0°C discharges are shown in Figures 4-6. Note the change of scale for the capacity axis on Figures 5 and 6. Although elevated temperature storage causes more degradation in the 0°C performance, the same general conclusions can be reached as for the 25°C discharges.

The discussion to this point has considered only the effects of elevated temperature storage at open circuit. Storage under 150 µA drain mitigated the voltage delay of the SAB cells, although the average discharge voltage was still well below that of the BP cells. The average capacities, including the amounts consumed during storage, were in all cases equal to or somewhat greater than comparable data taken on cells stored at open circuit, where available. In particular, the apparent 0°C capacities were higher by virtue of the additional amount consumed during the 30°C or 50°C storage period.

The performance of the 6 cells (BP with or without SO_2) that were tested fresh averages 14.9 Ah with a standard deviation of 0.45 Ah. The average discharge voltage was 3.41 V with a standard deviation of 0.02 V. We can normalize capacity by the volume of the cathode to eliminate cell-to-cell size variations in the data analysis. Using the normalized capacities, for cells stored both at open circuit and under load, a rate of self discharge is calculated for the 30 week storage period. Cells stored at 50°C and discharged at 25°C had approximately 5% less capacity than fresh cells. Storage at 30°C prior to 25°C discharge caused a loss of less than 1% of the capacity.

Complex Impedance and Microcalorimetry

We measure the complex impedance of the cells at intervals throughout the aging periods. We use the diameter of the high frequency semicircular component of the impedance spectrum to monitor the relative resistance of the passive film on the Li anode. While the film resistance does grow more quickly at higher temperature, its growth rate is not greatly affected by the carbon type or addition of SO_2 to the electrolyte. The influence of the initial Li surface condition when the cell is filled may be masking these other effects.

We also use microcalorimetry as a nondestructive means of sampling the cells. The SAB cells, which exhibit the poorest discharge performance, also exhibit the highest heat output. Table I presents sample data for measurements at 30°C and 50°C.

Table I

Identity	Temp. °C	Age Weeks	Avg. Heat Microwatts
BP	30	36	170
BP & SO_2	30	30	80
SAB	30	37	270
BP	50	30	100-200
BP & SO_2	50	30	200-300
SAB	50	30	500-600

Summary

The SNL-MR-D cells with a cathode blended of BP and SAB carbons perform superior to cells without BP in the cathode, both fresh and after accelerated aging studies. Cells using the BP/SAB cathode and a 1.0M $LiAlCl_4/SOCl_2$ electrolyte with or without SO_2 additive, when built as in-house prototypes, have an average fresh cell capacity of 14.9 Ah at 3.41 V at 25°C and a 6.25Ω load (~550 mA). The cells lost ~5% of capacity during 30 weeks storage at 50°C, and ~1% loss when stored at 30°C.

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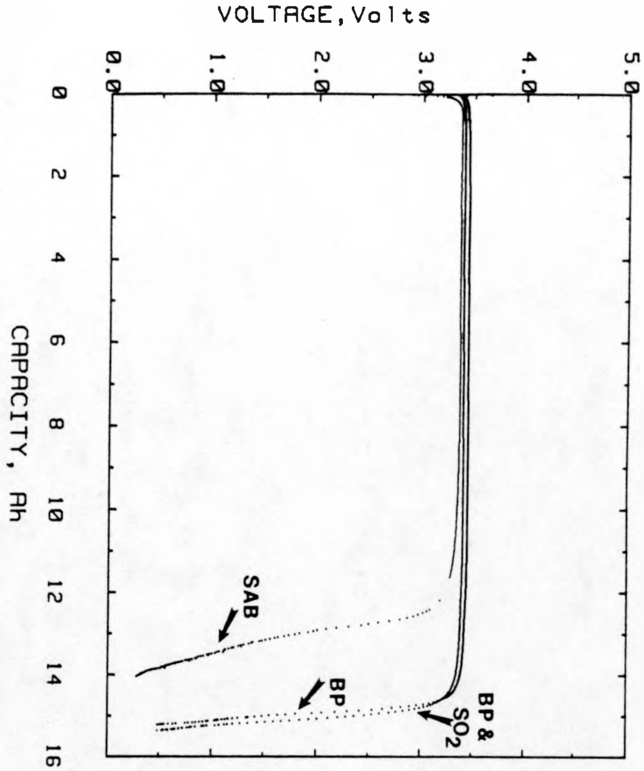

Figure 1. Fresh cells discharged at 25°C and 6.25 ohms.

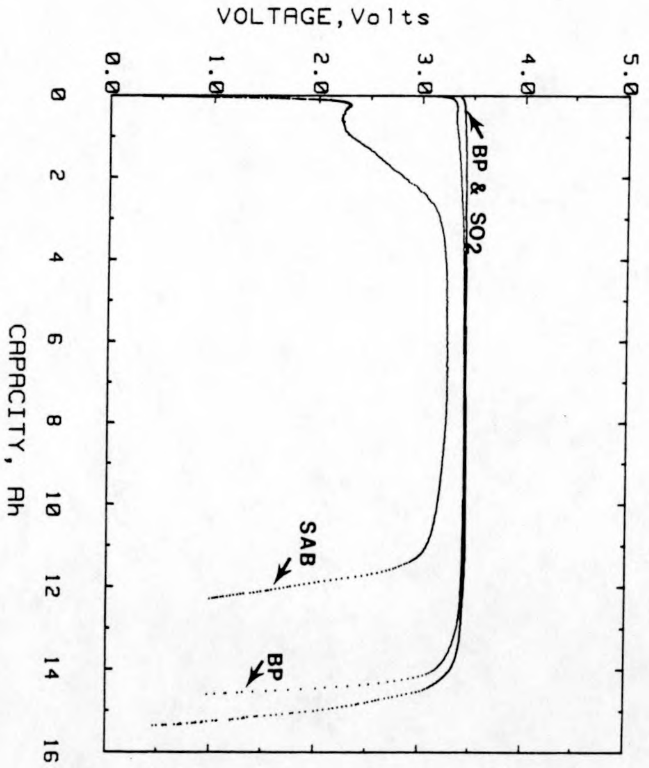

Figure 2. Cells aged at 30°C for 30 weeks, open circuit, and discharged at 25°C and 6.25 ohms.

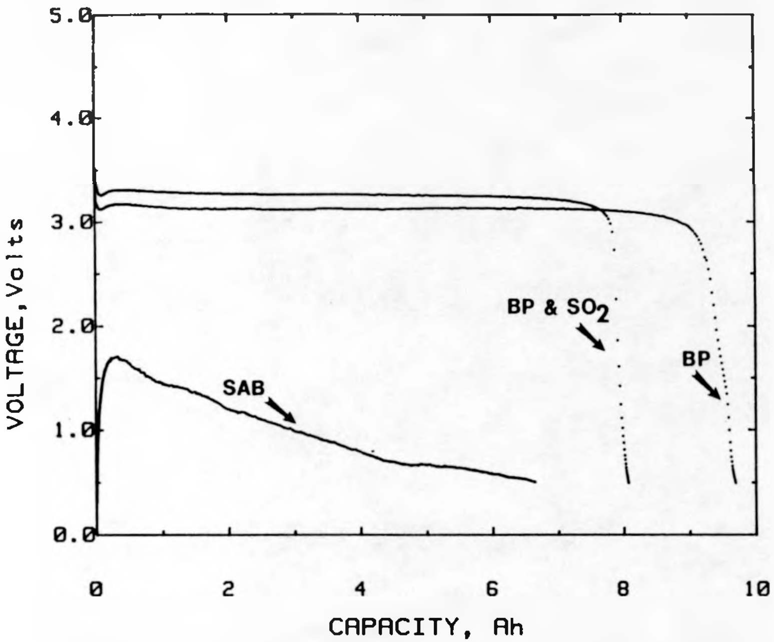

Figure 5. Cells aged at 30°C for 30 weeks, open circuit, and discharged at 0°C and 6.25 ohms.

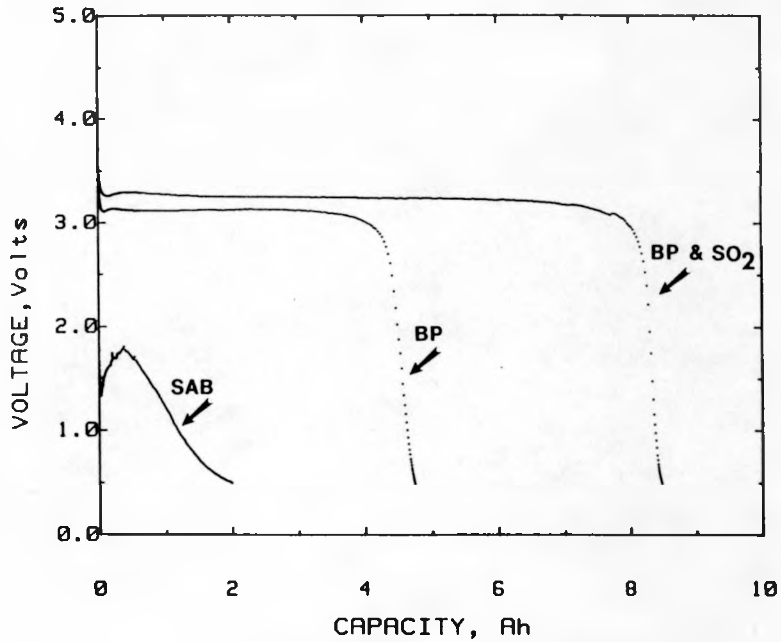

Figure 6. Cells aged at 50°C for 30 weeks, open circuit, and discharged at 0°C and 6.25 ohms.

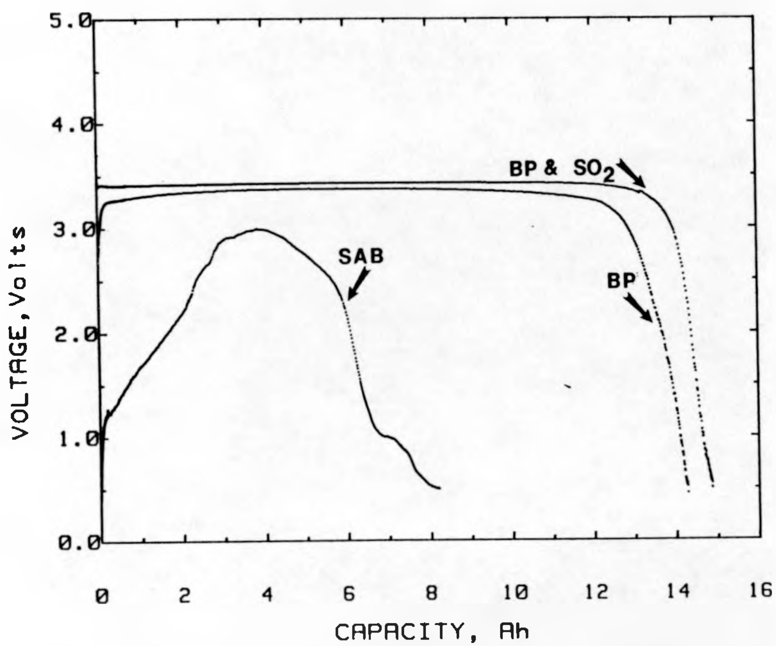

Figure 3. Cells aged at 50°C for 29 weeks, open circuit, and discharged at 25°C and 6.25 ohms.

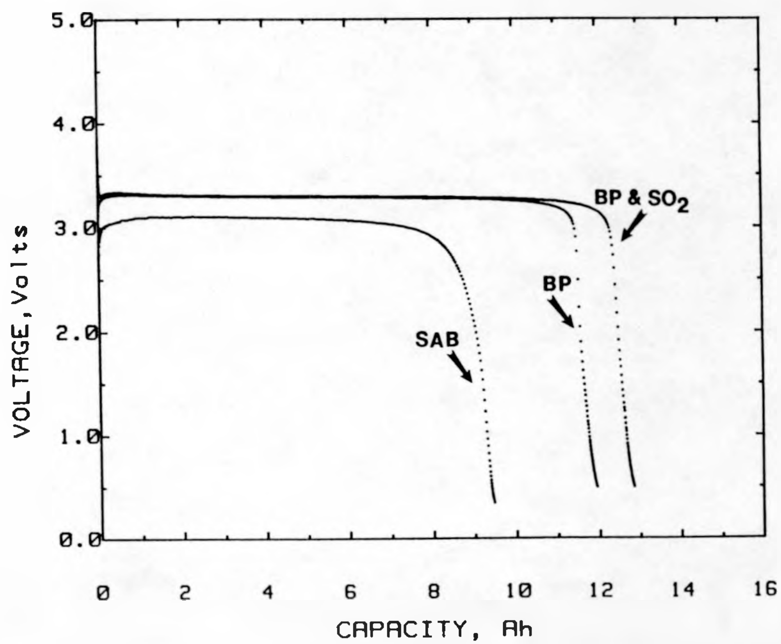

Figure 4. Fresh cells discharged at 0°C and 6.25 ohms.