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The technology of the Li/BrCl in $SOCl_2$ inorganic battery system: performance and self-discharge characteristics following long-term storage

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Investigations were conducted on Li/BrCl in $SOCl_2$ cells to determine both the performance and shelf life characteristics after storage for a period of one year at various temperatures. Room temperature discharge test results indicate that there is little self-discharge in those cells stored at either room temperature or at $-40°$ C. Even when the cells were subjected to elevated storage temperatures, the discharge results show that the cells exhibit a low self-discharge rate. However, cells stored at an elevated temperature do exhibit a decreased rate capability when compared to those results obtained from fresh cells. From the 56 ohm load discharge performance results, the self-discharge rate for cells stored at -40, 24, 50 and 72° C was calculated. Further, the activation energy over the temperature range was found to be 27.6 ± 1.7 kJ. Also, the self-discharge rate was monitored under light load conditions. The results for Li/BrCl in $SOCl_2$ D cells discharged under a current density of 2.38 to 0.016 mA cm^{-2}, show that the operationally induced self-discharge rate reaches a maximum of 4.5 μA cm^{-2} for cells discharged under a current density of 0.034 mA cm^{-2} and decreases to 2.9 μA cm^{-2} as the discharge current density decreases to 0.016 mA cm^{-2}. These data indicate that the self-discharge rate for cells discharged under very light loads may eventually approach that for cells stored under open circuit conditions.

1. Introduction

Investigations have been conducted on the performance and safety characteristics of the Li/BrCl in $SOCl_2$ system. It was found [1, 2] that these cells have high energy densities at low to medium discharge rates. Furthermore, properly designed cells are quite abuse-resistant under such conditions as short circuiting, forced overdischarge and a forced overdischarge/charge sequence.

Although preliminary studies on the storability characteristics of Li/BrCl in $SOCl_2$ cells were conducted [1], no detailed information was obtained for cells stored for extended periods of time, especially at elevated temperatures. Therefore, a study was initiated to investigate the performance and shelf life characteristics of cells stored for a period of one year at various temperatures. Li/BrCl in $SOCl_2$ C cells were used as test vehicles during these studies. From the data obtained from the stored cells, both the self-discharge rate at various temperatures and the activation energy of the system were calculated.

Further, a study to determine the effects of a low rate discharge on the self-discharge rate was conducted. Li/BrCl in $SOCl_2$ D cells were discharged at room temperature under various loads ranging from 10 to 1540 ohms. The realized capacities were obtained to a 2 V cutoff and the capacity loss was calculated using 15 Ah as the value for the nominal capacity. The effects of both low rate discharge and/or storage under open circuit conditions on the self-discharge rate are discussed in this article.

2. Experimental details

2.1. *Electrolyte preparation*

Details relative to the BrCl in $SOCl_2$ electrolyte

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preparation were given previously [1], A 6 : 1 mol ratio of $SOCl_2$: BrCl and an electrolyte composition of 1 mol dm^{-3} $LiAlCl_4$ in the codepolarizer were found to be the optimum composition according to studies performed in this laboratory.

2.2. *Electrode preparation*

The carbon electrodes contained 93 wt % Shawinigan acetylene black (50% compressed) and 7 wt % Telfon binder (TFE-fluorocarbon resin dispersion No. 30, DuPont). The current collectors for both the anode and cathode consisted of an expanded nickel screen (Exmet Corporation) which extended the entire length of each respective electrode. The separator material was a non-woven glass (Mead Corporation) with 6% binder. The anodes were prepared by pressing lithium ribbon (Foote Mineral Company) onto the nickel current collector.

2.3. *Cell fabrication*

All test cells were made by winding the lithium anode, the carbon cathode and two layers of non-woven separator into a cylindrical roll and packaging the roll into a 304L stainless steel can. The spirally wound C and D cells have a carbon electrode geometric surface area of 70 and 147 cm^2, respectively. Tabs on the anode current collectors were spot welded to the stainless steel case to ensure positive electrical contact. A lid consisting of a glass to metal seal and fill port was TIG welded to the can. Vacuum filling techniques were used to achieve an electrolyte fill volume of 12.5 and 23.5 cm^3 for C and D cells, respectively. All cell fabrication and filling processes were performed in a dry atmosphere (less than 0.5% humidity, $-50°$ C dew point).

2.4. *Test conditions*

Test cells were discharged under various resistive loads at room temperature ($24 \pm 3°$ C). For high and low temperature storage, the test cells were stored in either Thelco ovens at 50 and $72 \pm 3°$ C or a Revco ultra low cold chamber at $-40 \pm 3°$ C. The load voltages were measured through the use of a timed sequential electrometer coupled with a Hewlett Packard (HP85) computer. All realized capacities were obtained to a 2 V cutoff.

3. Results and discussion

Spirally wound Li/BrCl in $SOCl_2$ C cells were thermally equilibrated at room temperature after being stored for a period of 1 year at -40, 24, 50 and $72 \pm 3°$ C and discharged under constant loads of 10 to 56 ohms. The average performance results for stored cells discharged under 56 ohms loads are presented in Fig. 1. It appears that there is little self-discharge in those cells stored at either room temperature or at $-40°$ C. The realized capacity for fresh cells did not differ significantly from those cells stored at -40 and 24° C (7.36, 7.25 and 6.87 Ah, respectively). Even when the cells were subjected to elevated storage temperatures, the discharge results show that the cells exhibit a low self-discharge rate. For cells stored at 50 and 72° C for 1 year, the average realized capacities were 6.35 and 6.06 Ah, respectively. Cells stored at 72° C exhibited an increased initial polarization as well as a reduced current capability. Upon application of the 56 ohm loads, the voltage decreased rapidly and then increased during the next 3 min of discharge to a load voltage plateau of approximately 0.1 V lower than that observed for cells stored for one year at either ambient temperature or at $-40°$ C.

Figs. 2 to 4 show the performance characteristics for the stored cells discharged under constant loads of 30, 20 and 10 ohms, respectively. These results are quite similar to those obtained for cells discharged under 56 ohms. The results for cells stored at $-40°$ C show no significant differences in load voltage or realized capacity when compared to the performance characteristics for fresh cells. However, the results for cells stored at 24, 50 and 72° C also show that the realized capacity and rate capability of the cells are a function of both storage temperature and discharge rate. Cells stored at elevated temperatures exhibited a decreased rate capability, especially when discharged at relatively high rates. It is apparent that the effect of storage for the Li/BrCl in $SOCl_2$ C cells at elevated temperatures results in a loss of rate capability, but no significant loss in capacity for cells discharged under light loads. There is,

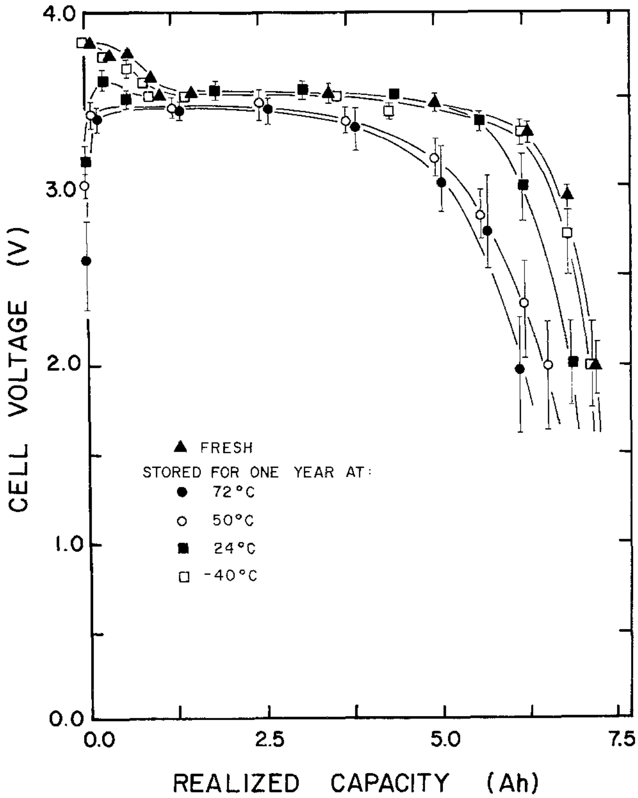

Fig. 1. Room temperature performance characteristics for 1 year old Li/BrCl in $SOCl_2$ C cells discharged under 56 Ω loads.

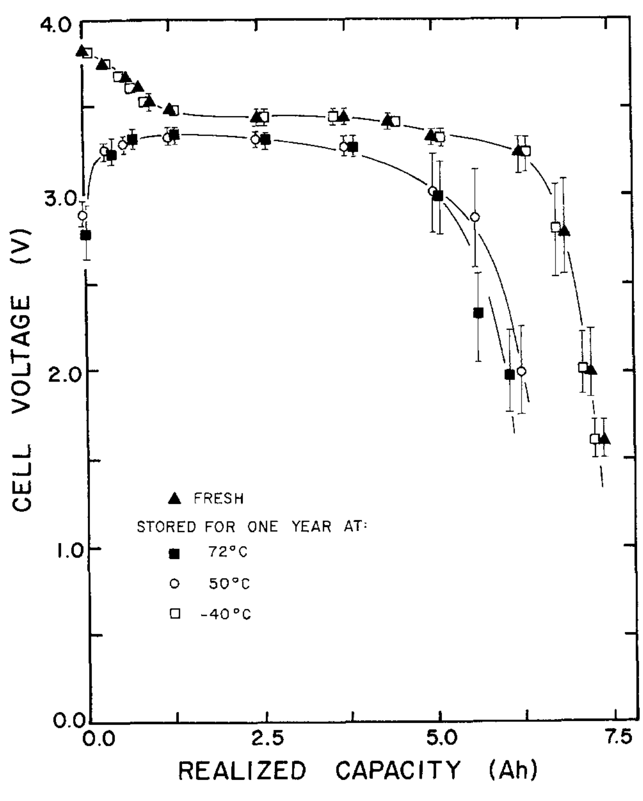

Fig. 2. Room temperature performance characteristics for 1 year old Li/BrCl in $SOCl_2$ C cells discharged under 30 Ω loads.

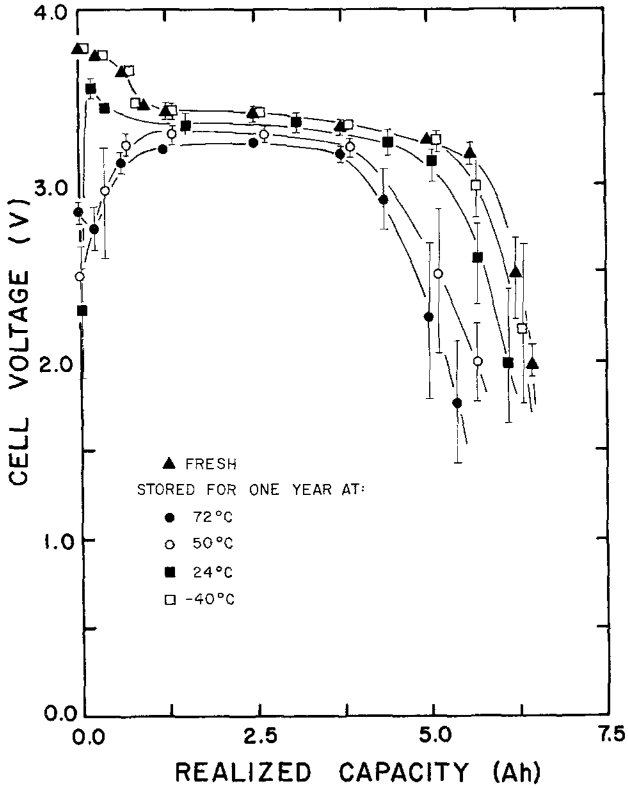

Fig. 3. Room temperature performance characteristics for 1 year old Li/BrCl in $SOCl_2$ C cells discharged under 20 Ω loads.

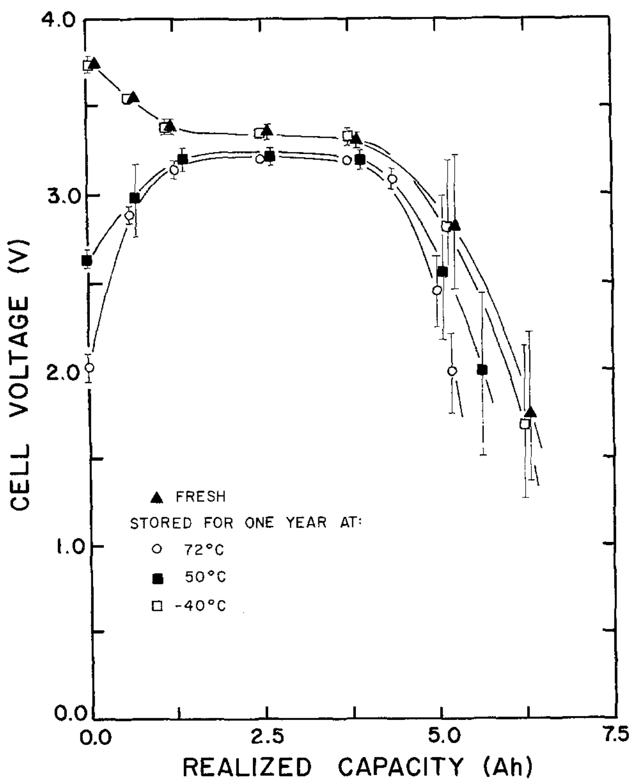

Fig. 4. Room temperature performance characteristics for 1 year old Li/BrCl in $SOCl_2$ C cells discharged under 10 Ω loads.

however, a resulting loss in capacity for cells discharged at medium to high rates.

It was also found that the variability in cell to cell performance increased with discharge rate. For example, cells discharged under a 10 ohm load showed a wider range in load voltage values near the end of life when compared to the results for cells discharged under constant loads of 56 ohms.

The intrinsic self-discharge rate could be masked by this variability in cell performance when cells were discharged under higher rates. To minimize these effects, calculations concerning self-discharge rates were based solely on capacities obtained from cells discharged under 56 ohm loads. This corresponds to a discharge current density of 0.9 mA cm^{-2}. The results of constant load, room temperature discharge tests for approximately 250 fresh and stored Li/BrCl in $SOCl_2$ C cells are summarized in Table 1. It can be seen that the rate of self-discharge is dependent upon the storage temperature. Values for the self-discharge rate range from a mean of 0.17 $\mu A\ cm^{-2}$ at − 40° C to 2.1 $\mu A\ cm^{-2}$ at 72° C. The variability in cell performance at each specific storage temperature represents a narrow band of realized capacities. However, performance anomalies were noted in certain lots of cells stored at 24° C for a period of 1 year. These cells exhibited an abnormally broad realized capacity band when discharged under constant loads of 56 ohms. For example, one particular group of cells exhibited a very wide range in realized capacity of 4.49 to 6.57 Ah. Test cells from these groups, including the cell which delivered 4.49 Ah, were destructively analysed following discharge. It was found that the Teflon insulator used at each end of the spirally wound anode and cathode assembly (providing electrical insulation of the electrodes from the case) showed signs of chemical reaction. It was also found that many of the insulators (Fig. 5), especially those from cells which exhibited a diminished realized capacity, became totally black. Further investigation revealed that the insulators were very brittle and exhibited increased electrical conductivity. Other lots of cells stored at 24° C showed less cell to cell performance variability and proportionately less insulator degradation than the above group of cells. Insulators from cells stored at − 40, 50 and 72° C were also examined. Little or no degradation was noted on the insulators from cells stored at − 40° C. Although varying degrees of attack were evident on samples taken from cells stored at 50 and 72° C, it appeared that the extent of insulator degradation was greater under room temperature storage conditions when compared to that for cells exposed to elevated temperatures. Thus, this material incompatibility may have resulted in abnormally high self-discharge rates, especially for those cells stored at 24° C.

Calculations of the activation energy excluded these data obtained from groups of cells which exhibited extreme performance anomalies. The

Table 1. The self-discharge rate of 1 year old Li/BrCl in $SOCl_2$ C cells as a function of storage temperature

Storage conditions		*Load* (Ω)	*Range in the values of realized capacity to 2 V* (Ah)	*Range in values for the self-discharge rate** ($\mu A\ cm^{-2}$)
Time (y)	*Temperature* (° C)			
0 (fresh cells)	24	56	7.18–7.49	–
1	72	56	5.78–6.32	2.6–1.8
1	50	56	6.06–6.71	2.1–1.1
1	24	56	6.28–7.07	1.7–0.48
1	24	56	(4.49–7.07)†	(4.7–0.48)‡
1	−40	56	7.09–7.30	0.38–0.11

* Current density values based upon 96.5 cm^2 lithium electrode geometric surface area (3.8 cm × 12.7 cm × 2 sides).
† Includes data from all cells which exhibited an excessive amount of chemical attack on the internal Teflon insulators.
‡ The data comprising this range in self-discharge values were not used in subsequent calculations for the energy of activation.

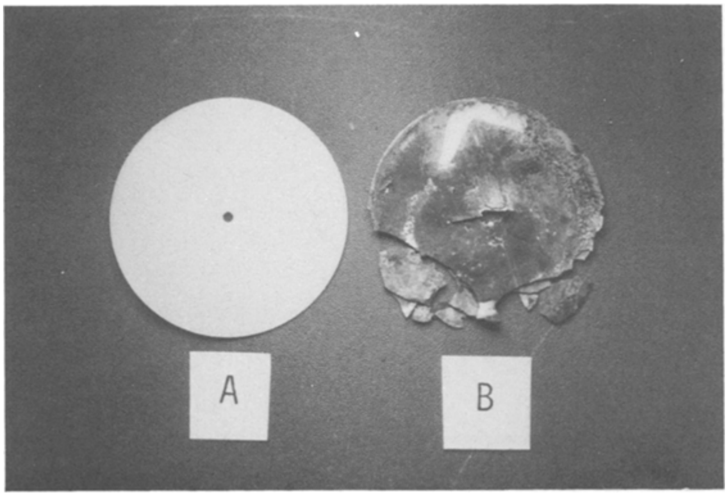

Fig. 5. A photograph of the internal Teflon insulator: (a) a virgin insulator; (b) a typical insulator from a cell which had been stored for 1 year at room temperature prior to discharge.

Arrhenius plot of the rate of self-discharge at various storage temperatures is shown in Fig. 6. The activation energy, as calculated from the least squares slope of the region between 72 and − 40° C, is 27.6 ± 1.7 kJ.

Experimental cells were fabricated to determine the compatibility of various types of Teflon with the codepolarizer. One set of these cells contained FEP Teflon insulators. After 3 months storage at − 40, 24, 50 and 72° C, these insulators were examined for signs of chemical attack. No significant degradation was evident on the insulators stored over the temperature range. Therefore, Li/BrCl in $SOCl_2$ C cells were fabricated using FEP insulators. These cells are presently being stored under open circuit conditions at − 40, 24, 50 and 72 ± 3° C and will be tested in accordance with the above at various storage intervals. Based upon these preliminary results obtained from cells containing FEP Teflon insulators, one may speculate that the self-discharge rate may actually be lower under all storage temperature conditions.

Although cells stored under open circuit conditions exhibited a low self-discharge rate, it was noted that cells discharged under relatively low rates showed some additional loss in capacity. Therefore, investigations in this laboratory have

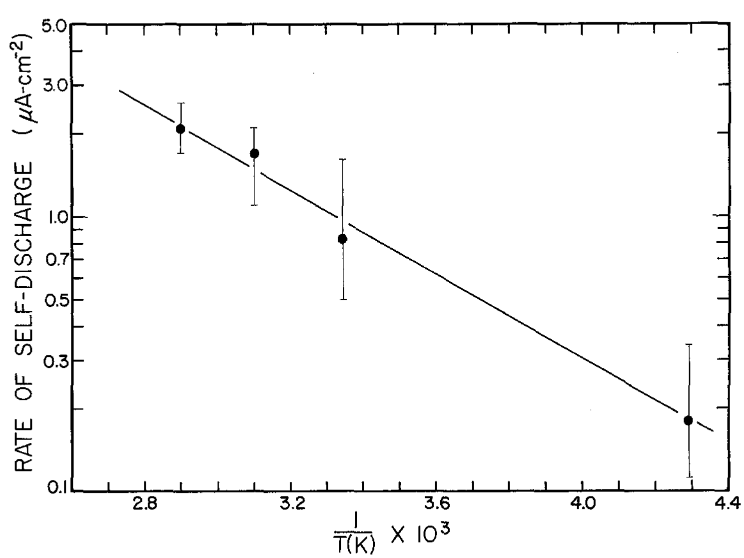

Fig. 6. The Arrhenius plot of the rate of self-discharge at various storage temperatures.

Table 2. Comparison of the constant load discharge characteristics for Li/BrCl in $SOCl_2$ D cells

Load (Ω)	*Approximate current* (mA)	*Discharge current density** (mA cm^{-2})	*Realized capacity to 2 V* (Ah)	*Self-discharge current density*† (μA cm^{-2})
10	350	2.38	14.8	–
20	175	1.19	15.1	–
75	50	0.34	14.9	–
332	10	0.068	14.1	3.7
681	5	0.034	12.9	4.5
1540	2.3	0.016	11.9	2.9

* Current density values based upon 147 cm^2 carbon electrode geometric surface area (4.9 cm × 15.0 cm × 2 sides).
† Current density values based upon 183 cm^2 lithium electrode goemetric surface area (4.9 cm × 18.7 cm × 2 sides).

also been concerned with the self-discharge characteristics of Li/BrCl in $SOCl_2$ D cells during the low rate discharge. Li/BrCl in $SOCl_2$ D cells were discharged at room temperature under various loads ranging from 10 to 1540 ohms.

The results for the constant load discharge characteristics of Li/BrCl in $SOCl_2$ D cells are summarized in Table 2. Throughout the discharge current density range of approximately 2.38 to 0.34 mA cm^{-2}, no significant difference in realized capacity exists. However, as this current density decreases, the capacity also gradually decreases until a capacity of 11.9 Ah is realized at the lowest discharge current density of 0.016 mA cm^{-2}. Using 15 Ah as the nominal capacity for the cells, the self-discharge rate for cells discharged under 332, 681 and 1540 ohm loads was calculated. The average capacity loss for cells discharged under a current density of 0.068 mA cm^{-2} (332 Ω) was 0.9 Ah. This corresponds to an operationally induced self-discharge rate of 673 μA or 3.7 μA cm^{-2} of anode surface area over the 1337 h discharge period. Similar calculations for cells discharged under current densities of 0.034 and 0.016 mA cm^{-2} (681 and 1540 ohms, respectively) show a self-discharge rate of 827 μA (4.5 μA cm^{-2}) and 584 μA (2.9 μA cm^{-2}), respectively. Similar data for D cells discharged under loads of 3300 and 6800 ohms are not yet available. However, the data for D cells discharged over the current density range of 0.068 to 0.016 mA cm^{-2} do show that there is a continuous loss in capacity. This may be attributed to the persistent chemical corrosion of the fresh lithium surface due to the slow mechanical disruption of the LiCl film under the low discharge rates. However, these data also showed that the self-discharge rate increases to a maximum value of approximately 4.5 μA cm^{-2} under a discharge current density of 0.034 mA cm^{-2} and decreases to 2.9 μA cm^{-2} at a 0.016 mA cm^{-2} discharge rate. Consequently, we reason that the self-discharge rate for cells discharged under very light loads may eventually approach those for cells stored under open circuit conditions.

In conclusion, performance results for cells stored one year under open circuit conditions at − 40, 24, 50 and 72° C have shown that the self-discharge rates are approximately 0.17, 0.81, 1.7 and 2.1 μA cm^{-2}, respectively. Especially noteworthy are the low self-discharge rates at the elevated temperatures (50 and 72° C). It has also been shown that the self-discharge rate reaches a maximum of 4.5 μA cm^{-2} for Li/BrCl in $SOCl_2$ D cells discharged under 681 ohm loads and decreases to 2.9 μA cm^{-2} for cells discharged under lighter loads. Eventually the values for the self-discharge rate for cells under the lightest load may approach those for cells stored under open circuit conditions. The results of this investigation have shown that Li/BrCl in $SOCl_2$ is a practical system which has a low self-discharge rate and excellent shelf life characteristics over a wide temperature range.

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