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Improved Li/BCX Primary Cells for Space Applications

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Abstract

Li/BCX (bromine chloride in thionyl chloride) primary cells have been qualified for flight aboard the space shuttle for over fifteen years. These cells provide high energy density while maintaining an excellent safety record. Recently, changes to the electrolyte have resulted in an improved Li/BCX II system with a lower self-discharge rate. The use of low molarity electrolytes in programs unique to NASA have improved the safety hazards tolerance of these cells while maintaining or increasing their energy density.

Introduction

Wilson Greatbatch Ltd. develops and manufactures lithium cells and battery packs for the medical, space, industrial and commercial markets. Many applications still require the use of lithium primary batteries with a high energy density. This is especially true for space applications.

During the past fifteen years, the Li/BCX (bromine chloride in thionyl chloride) primary battery system has been qualified for flight aboard the space shuttle. The excellent safety record of the system, high open circuit voltage of 3.9 volts, good low temperature performance, specific energy of 472 Wh/kg and energy density of 1,035 Wh/L make it an attractive power supply for a variety of applications (1, 2, 3). Presently, Li/BCX C, D and DD cells are qualified power sources for the video cameras, cassette tape data recorders, hand warmers in gloves, helmet lights, AN/PRC-112 survival radio and extravehicular mobility unit/personal life support system used in every shuttle flight.

The Li/BCX system exhibits excellent voltage retention when stored for several years at room temperature. Data will be presented to show that advances made to the Li/BCX II system have improved the self-discharge previously observed. In addition, the restart capability and energy density of the system have been maintained or improved, particularly at lower discharge rates. In programs unique to NASA, the use of lower molarity electrolytes has been investigated and shown to enhance cell safety. Li/BCX II cells are now tolerant to a fifty milliohm short-circuit at room temperature and can be exposed to temperatures as high as 140°C without leaking. Despite the reduced salt concentration used in the electrolyte, the high, moderate and low rate discharge capacity goals of the various programs were still achieved.

Chemistry and Design Features

All cells were spirally wound and contained in stainless steel cases and lids that have corrosion resistant glass-to-metal seals. Battery grade lithium was laminated onto metal grids to form the anode current collector assembly. The cathode current collector assembly was fabricated by sheeting a mixture of carbon black and polytetrafluoroethylene binder onto expanded metal. The separator was a nonwoven glass fiber paper. The two electrodes and the separator were wound together and inserted into the stainless steel case. The anode lead was then welded to the case, resulting in a case negative configuration, and the cathode lead was welded to the positive pin feedthrough in the header. The BCX and BCX II electrolytes were prepared by forming a suitable electrolyte salt in-situ in the bromine chloride in thionyl chloride solution. After filling with the BCX or BCX II catholyte, cells were hermetically sealed by welding a stainless steel ball over the fill hole.

Characteristics of the Li/BCX System

The Li/BCX system offers several features which make it the power system of choice for several space applications. In addition to having a good safety record and high proven reliability, the system offers a power density as high as 95 W/l and has an energy density of 1035 Wh/l. Additionally, cells are rated for operation at temperatures in the range -55°C to 72°C. When necessary, modifications to the system allow for operation at temperatures approaching -100°C. Historically, the Li/BCX system has been characterized by a self-discharge rate of 3-15%/year.

To fully characterize the Li/BCX system, a large number of D cells were built and stored at room temperature for several years. After initially testing fresh cells under loads ranging from 0.5 ohms to 3010 ohms, additional cells were periodically removed from storage after 6, 12, 24 or 36 months and fully discharged under the same spectrum of loads. As shown in Figure 1, the mid-life operating voltage of the Li/BCX system remained stable even after three years of room temperature storage, varying by less than 200 millivolts. Furthermore, cells discharged under a 1 ohm load maintained a mid-life operating voltage of over 3.0 volts.

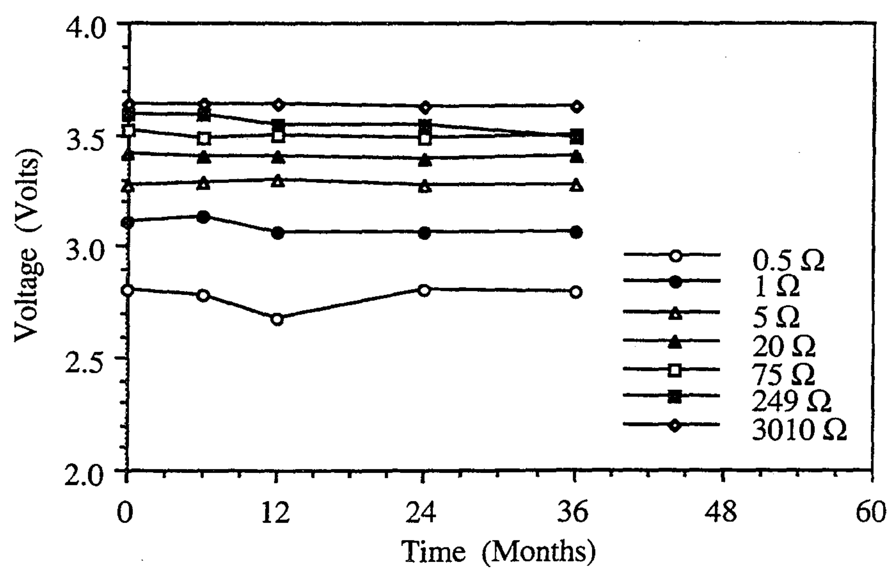

Figure 1: Voltage retention of Li/BCX D cells at 50% depth of discharge.

The capacity retention of Li/BCX D cells over a three year period is shown in Figure 2. The 2.0 volt discharge capacity was measured and recorded for cells that were discharged after 0, 6, 12, 24 or 36 months of room temperature storage. When discharged under loads ranging from 5 ohms to 249 ohms, fresh cells generally provided 13.5 to 15.0 Ah. Over the three year storage period, the cell capacity declined to about 11.0 to 12.0 Ah, representing a yearly self-discharge rate of approximately 9%. As expected, fresh cells that were discharged under a considerably heavier load of 1 ohm or 0.5 ohms provided less capacity due to increased cell polarization. Cells discharged under a 3010 ohm load, however, also provided lower capacity.

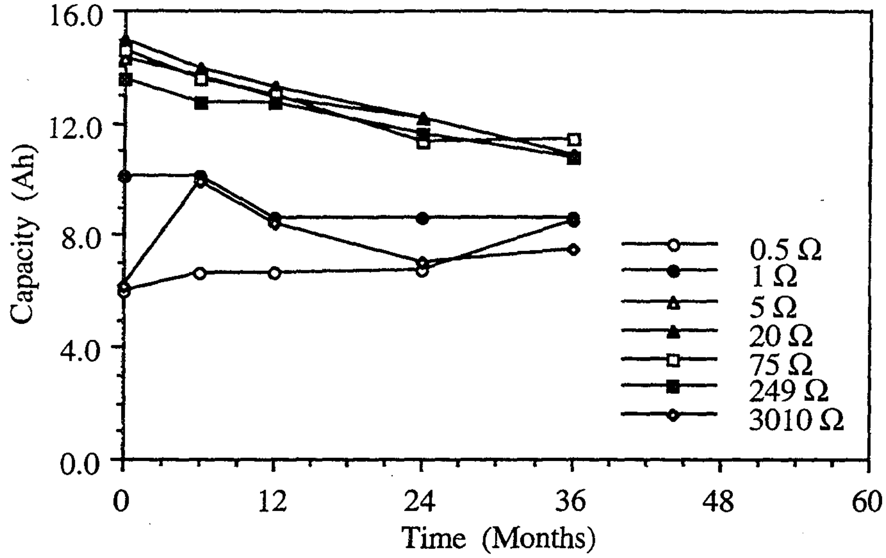

Figure 2: Capacity retention of Li/BCX D cells to 2.0 volts.

Microcalorimetry, in which cell heat dissipation is measured under load or on open circuit voltage, has proven to be a useful tool in estimating the lifetime of Li/BCX cells (4). Recently, modifications and improvements to the electrolyte have resulted in the development of BCX II cells which are characterized by lower self-discharge as measured via microcalorimetry and confirmed via discharge test. As shown in Figure 3, when stored at room temperature over a four year period, Li/BCX II D cells exhibited approximately forty percent of the heat dissipation that Li/BCX D cells exhibited. This manifests itself in a much slower degradation in open circuit voltage as shown in Figure 4. While the open circuit voltage of Li/BCX D cells decreased from 3.95 volts to 3.67 volts over a period of eighteen months, the open circuit voltage of Li/BCX II D

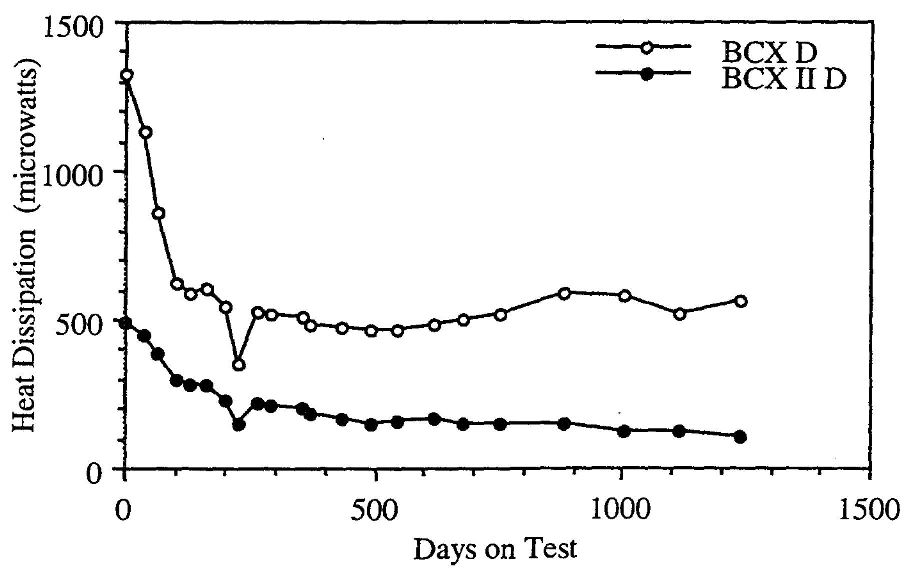

Figure 3: Heat dissipation of Li/BCX D and Li/BCX II D cells.

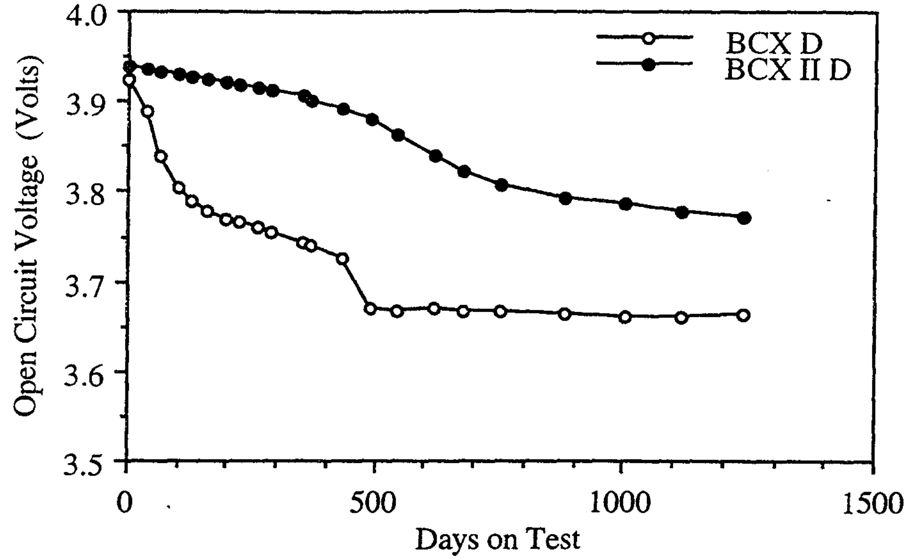

Figure 4: OCV stability of Li/BCX D and Li/BCX II D cells.

cells remained at or above 3.75 volts after four years.

Complementing the microcalorimetry results are discharge results for fresh Li/BCX D and Li/BCX II D cells. In Figure 5, the 2.0 volt discharge capacity obtained for cells tested at room temperature under loads ranging from 0.5 ohms to 3010 ohms is shown. Discharge capacity for the Li/BCX system and the Li/BCX II system is comparable under loads ranging from 0.5 ohms to 20 ohms. At 75 ohms and 249 ohms, discharge capacity is higher for the Li/BCX II system, validating the data obtained via microcalorimetry. Discharge tests under a 3010 ohm load remain in

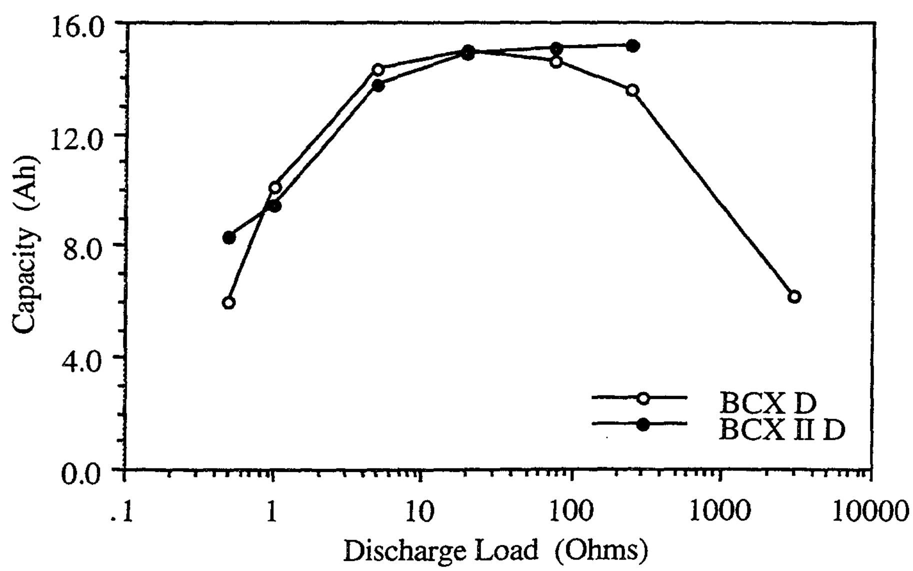

Figure 5: Comparison of discharge capacity to 2.0 volts for fresh cells.

progress; however, capacity obtained to date with the Li/BCX II system has already surpassed that previously obtained with the Li/BCX system.

Voltage delay is a common occurrence associated with liquid cathode primary lithium cells. The phenomenon is attributed to increased thickness of the lithium passivation layer which results in increased cell impedance. During application of a discharge load, the cell voltage may be initially depressed before recovering to a steady-state value. The voltage delay phenomenon becomes more pronounced when cells are stored at elevated temperature or for long periods of time and subsequently discharged at low temperature and high current.

Comparisons were made of the room temperature voltage delay characteristics of Li/BCX D and Li/BCX II D cells discharged under a 4 ohm load. The results are shown in Figures 6 through 9 for fresh cells and for cells previously discharged to 10%, 30% and 60% depth of discharge, respectively. For fresh cells, as shown in Figure 6, little difference existed between the voltage of Li/BCX and Li/BCX II cells.

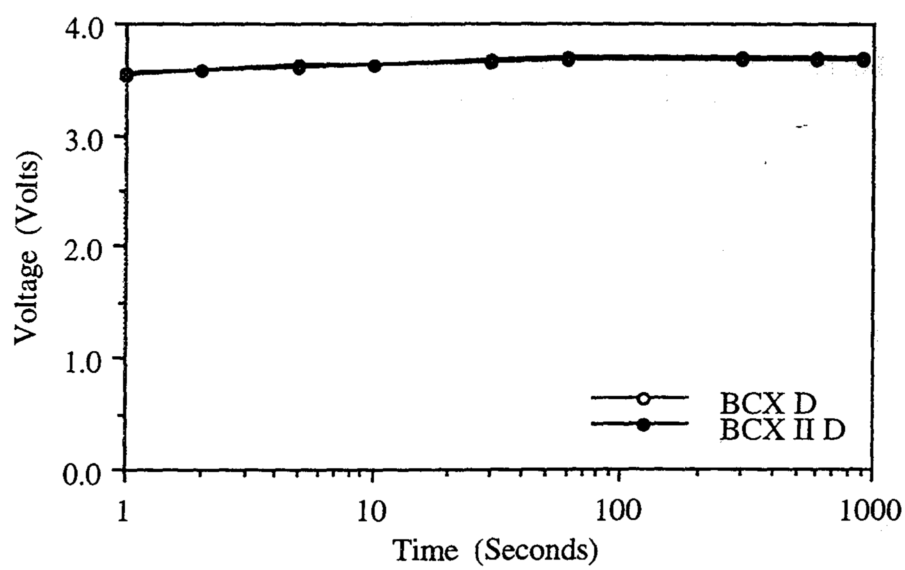

Figure 6: Room temperature voltage delay of fresh cells under 4 ohm load.

As shown in Figure 7, differences in voltage began to emerge at 10% depth of discharge. The Li/BCX II D cells exhibited a slightly higher voltage during the first five minutes of discharge; however, the voltage of both systems remained above 3.0 volts following application of the discharge load. In Figure 8, significant differences existed between the two systems at 30% depth of discharge. Whereas the voltage of Li/BCX II D cells remained above 3.0 volts, that of the Li/BCX D cells was depressed below 2.0 volts for the initial thirty seconds of the test and did not reach 3.0 volts during the first fifteen minutes of discharge. When restarted after 60% depth of discharge, Li/BCX D cells remained between 2.3 volts and 2.6 volts for the initial fifteen minutes of the test. Although the Li/BCX II D cell voltage declined below 2.0 volts during the initial ten seconds of test, it surpassed the voltage of the Li/BCX system within thirty seconds and ultimately recovered to above 3.0 volts within five minutes.

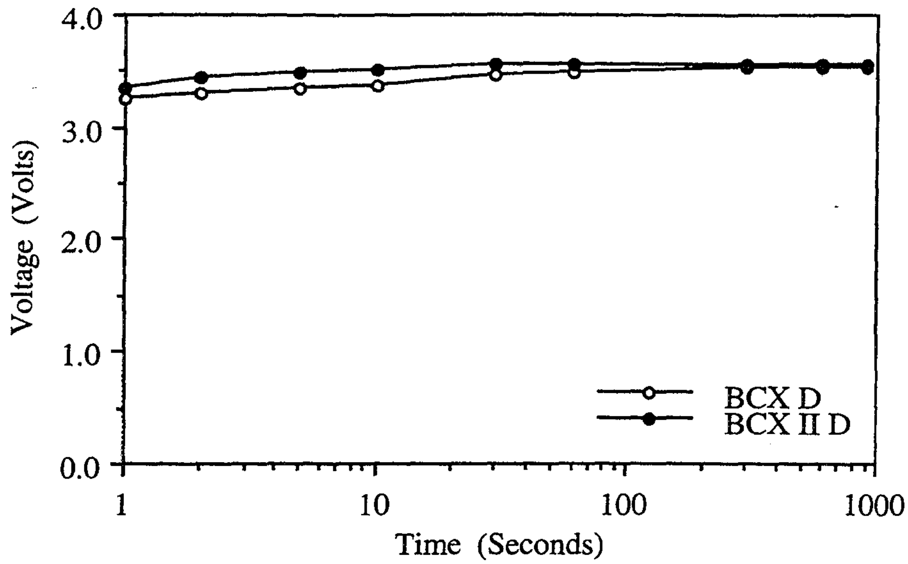

Figure 7: Room temperature voltage delay under 4 ohm load of cells at 10% depth of discharge.

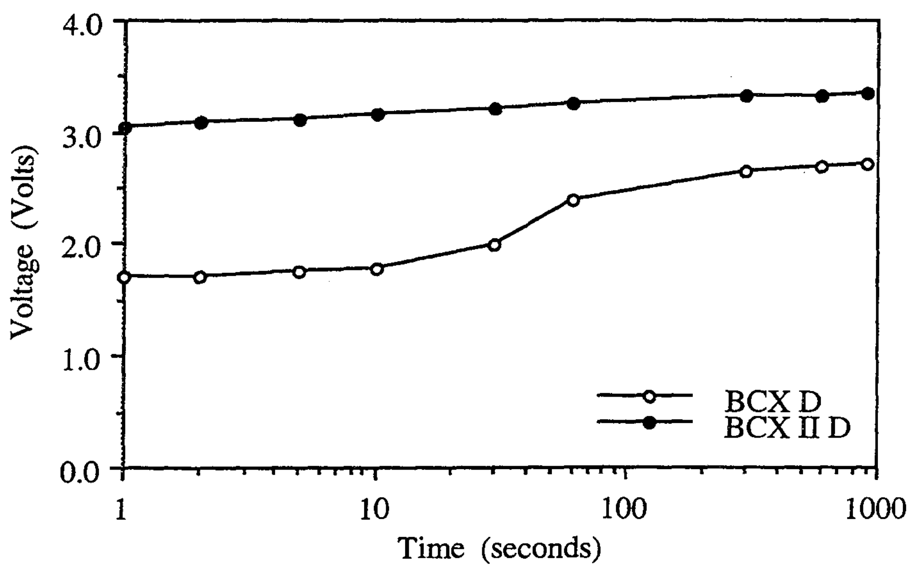

Figure 8: Room temperature voltage delay under 4 ohm load of cells at 30% depth of discharge.

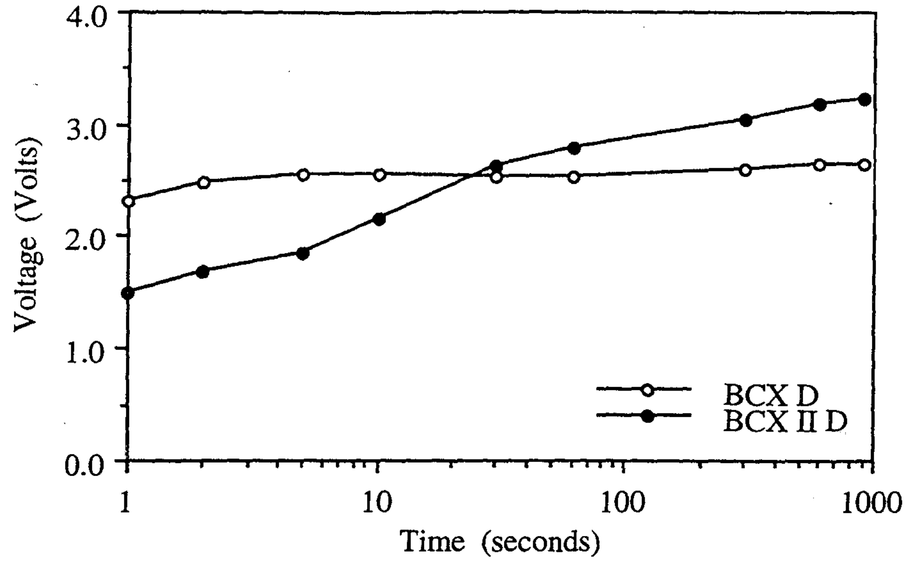

Figure 9: Room temperature voltage delay under 4 ohm load of cells at 60% depth of discharge.

Improved Cells for Space Applications

Wilson Greatbatch Ltd. and NASA have embarked on a series of development efforts aimed at maintaining or increasing the rate capability, capacity and temperature tolerance of Li/BCX cells while increasing the short-circuit hazards tolerance (5, 6, 7). To achieve these objectives, low molarity Li/BCX II cells including 0.6 M Li/BCX II C cells, 0.4 M Li/BCX II D cells and 0.6 M Li/BCX II DD cells were developed for present and future applications.

A primary goal for the next generation of cells is to be tolerant of a fifty milliohm external short-circuit while maintaining internal continuity and not having cells leak, vent or rupture. Short-circuit tests were conducted on low molarity Li/BCX II cells at room temperature using the designated angle iron as specified in NASA document number EP5-83-025 Rev. G. The test results are presented in Table 1. The 0.6 M Li/BCX II C cell exhibited a peak current of up to 22.5 amps and a peak temperature as high as 85.5°C. The 0.4 M Li/BCX II D cell and the 0.6 M Li/BCX II DD cell exhibited peak currents of 22.0 amps and 33.3 amps, and peak temperatures of 86.5°C and 100.0°C, respectively. None of the 0.6 M Li/BCX II C cells or the 0.4 M Li/BCX II D cells leaked, vented or ruptured as a result of these tests; however, a few of the 0.6 M Li/BCX II DD cells were observed to leak or vent mildly at the glass to metal seal.

Table 1. Fifty Milliohm Short-Circuit Tolerance of Low Molarity Li/BCX II Cells.

	Peak Current (Amps)	Peak Temp. (°C)	Physical Changes
0.6 M C Cell	19.2 - 22.5	59.0 - 85.5	None
0.4 M D Cell	16.0 - 22.0	77.0 - 86.5	None
0.6 M DD Cell	26.0 - 33.3	85.2 - 100.0	Mild Vent

The temperature tolerance of low molarity Li/BCX II C, D and DD cells was determined by exposing fresh cells, cells discharged to 2.0 volts or lower, and cells subjected to a fifty milliohm short- circuit test to temperatures in the range of 100°C to 160°C at 10°C exposure intervals. The test results are reported in Table 2. The temperature tolerance of all three types of cells was maintained at or above 100°C, nearly 30°C above the maximum temperature rated for use. The 0.6 M Li/BCX II C cells were tolerant to 140°C without leaking at the glass-to-metal seal.

Table 2. Temperature Tolerance of Low Molarity Li/BCX II Cells.

	Minimum Leakage Temperature
0.6 M C Cell	140°C
0.4 M D Cell	125°C
0.6 M DD Cell	100°C

The specific attributes of the Li/BCX and Li/BCX II systems make them attractive for use in a number of space applications. Accordingly, NASA may use the same cell for a variety of applications and each application may require that a specific capacity be obtained under a particular test regime. When designed, each type of cell may be required to meet minimum capacity requirements under various discharge loads. This allows the cell to be used interchangeably among the various programs and applications.

The capacity requirements for the 0.6 M Li/BCX II C cell are shown in Table 3. When discharged at room temperature under a 6 ohm load, cells are expected to provide a mean discharge capacity of 4.0 Ah. When discharged under a 10 ohm or 75 ohm load, cells are expected to provide a capacity of 5.0 Ah and 6.0 Ah, respectively. The low molarity cell provided 4.94 Ah, 5.38 Ah and 7.24 Ah to 2.0 volts when discharged under a 6 ohm, 10 ohm or 75 ohm load, satisfying the various program requirements.

Table 3. 0.6 M Li/BCX II C Cell Capacity Summary.

Discharge Load (Ohms)	Requirement (Ah)	Achieved (Ah)
6	4.00	4.94
10	5.00	5.38
75	6.00	7.24

The 2.0 volt capacity requirements for the 0.4 M Li/BCX II D cell and for the 0.6 M Li/BCX II DD cell are shown in Tables 4 and 5 along with the capacity achieved. The 0.4 M Li/BCX II D cells provided 10.0 Ah and 12.3 Ah when discharged at room temperature under a 10 ohm or 20 ohm load, satisfying the program requirements of 10.0 Ah. The 0.6 M Li/BCX II DD cell was required to provide 22.0 Ah at room temperature when discharged under a 1.5 ohm load, 25.0 Ah when discharged under a 2.5 ohm load and 27.0 Ah when discharged under a 10 ohm load. The data provided in Table 5 indicate that these objectives were achieved. The mean capacity delivered to 2.0 volts was recorded as 28.7 Ah, 32.3 Ah and 35.6 Ah, respectively.

Table 4. 0.4 M Li/BCX II D Cell Capacity Summary.

Discharge Load (Ohms)	Requirement (Ah)	Achieved (Ah)
10	10.0	10.0
20	10.0	12.3

Table 5. 0.6 M Li/BCX II DD Cell Capacity Summary.

Discharge Load (Ohms)	Requirement (Ah)	Achieved (Ah)
1.5	22.0	28.7
2.5	25.0	32.3
10.0	27.0	35.6

Development of the Li/BCX II system coupled with the use of low molarity electrolytes has led to the development of improved lithium primary cells for future space missions. As shown in Table 6, the specific energy and energy density of DD cells has been increased from 472 Wh/kg and 1035 Wh/l to 560 Wh/kg and 1256 Wh/l, an improvement of more than 18.5%. Additionally, the self-discharge rate of the system is projected to decrease from 3-15%/year to 1-3%/year, further improving the reliability and attractiveness of the system.

Table 6. DD Cell Capacity Comparison.

	1.14 M Li/BCX DD Cell	0.6 M Li/BCX II DD Cell
Specific Energy	472 Wh/kg	560 Wh/kg
Energy Density	1035 Wh/l	1256 Wh/l
Self-Discharge	3-15%/Year	1-3%/Year

Conclusions

The Li/BCX primary system offers stable voltage and high capacity after several years of storage. Recent improvements to the system have led to lower heat dissipation, resulting in a more stable open circuit voltage, a lower self-discharge rate and improved voltage delay characteristics. Low molarity Li/BCX II C, D and DD cells have been developed to meet the requirements of future space applications. The short-circuit hazards tolerance of these cells has been improved and the temperature tolerance has been maintained. The specific energy and energy density of low molarity Li/BCX II cells have been increased while the self-discharge rate is projected to decrease markedly.

References

1. C. C. Liang, P. W. Krehl and D. A. Danner, Journal of Applied Electrochemistry, 11, 563 (1981).

2. R. M. Murphy, P. W. Krehl and C. C. Liang, in Proceedings of 16th Intersociety Energy Conversion Engineering Conference, p. 97 (1981).

3. P. W. Krehl and C. C. Liang, Journal of Applied Electrochemistry, 13, 451 (1983).

4. E. S. Takeuchi, S. M. Meyer, and C. F. Holmes, Journal of Electrochemical Society, Vol. 137, No. 6, p. 1665 (1990).

5. P. J. Size, E. S. Takeuchi, Lithium D-Cell Study, Final Report, March 1993 (contract number NAS9-18395).

6. D. M. Spillman, N. M. Waite, E. S. Takeuchi, NASA Flight C Cell Development Program, Final Report, April 1996 (purchase order number T-5789T).

7. D. M. Spillman, N. M. Waite, E. S. Takeuchi, NASA Flight DD Cell Development Program, Final Report, October 1997 (purchase order number T-3193V).

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