Bulk thermal capacity determination for Li/BCX and Li/SOCl₂ cells

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Abstract

The bulk heat capacities of Li/BCX and Li/SOCl₂ cells were determined at 0 and 100% depth-of-discharge for 2.0 V cut-off voltage, in the temperature range 0 to 60 °C by a method that did not involve the destruction of the cell nor the contact of cell with a liquid. The heat capacity of Li/BCX cell is an important parameter for the design of a thermal control system for Li/BCX batteries. The heat capacities are found to be dependent on state-of-charge — increasing with depth-of-discharge. The Li/BCX DD-cell has a lower heat capacity (0.154 to 0.201 cal/(g K)) than a high rate Li/SOCl₂ D-cell (0.191 to 0.221 cal/(g K)). The results obtained by this method compare favorably well with results reported in the literature through other methods. The bulk heat capacities of the cells did not change significantly in the temperature range 0 to 60 °C.

Background

The high open-circuit potential, wide temperature of operation, high capacity and energy density are some of the qualities that make the Li/BCX cell very attractive [1]. There is a need therefore, to understand and characterize the thermal behavior of Li/BCX cells. One of the important parameters needed in a thermal analysis of a cell is the specific heat capacity. This parameter measures the capacity of a material to retain and/or allow heat transport through it. In ref. [2], it was demonstrated that measured heat capacities of batteries correlate well with the heat generated from the cells when discharged in an insulated environment (adiabatic discharge). Thus, the bulk heat capacity of a cell is an indication of the amount of heat it can generate when discharged adiabatically. Furthermore, to be able to predict the temperature distribution within a cell, the thermal conductivities of the cell materials (e.g. for distributed system modeling) or the bulk heat capacity of the cell (e.g. for lumped parameter modeling) must be known. Such thermal models will be helpful in the design of an appropriate thermal control system for large modular Li/BCX batteries projected for future NASA applications such as the Assured Crew Return Vehicle (ACRV) and Heavy Lift Launch Vehicle (HLLV).

Except for the presence of BrCl in Li/BCX cell, the basic components of both Li/BCX and Li/SOCl₂ cells are the same. However, the Li/BCX and Li/SOCl₂ cells

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are known to show different thermal characteristics [1]. Unfortunately, there is no known method for correlating the thermal data on the Li/SOCl$_2$ cells reported in the literature to those of Li/BCX cells except to determine them. It is thus imperative that accurate fundamental properties of the Li/BCX cell be known for a realistic thermal analysis of the system.

Kubow et al. [3], determined the thermal capacities of different sizes of Li/BCX cells by calorimetry. Previously, Takeuchi et al. [2] had presented results on the heat capacity of Li/BCX D-cell determined by both calorimetry and adiabatic discharge. Although some discrepancies were found in the two methods used, an average value of 0.25 cal/(g K) and 0.203 cal/(g K) were respectively determined by the adiabatic discharge method and calorimetric approach for the Li/BCX D-cell. A comparison of their experimental results with a theoretical model results (based on the contribution made by each cell component), showed that the experimental values were slightly higher than the model predictions. The experiments were carried out at a single temperature and thus their results cannot show the effects of temperature on the cell thermal properties. Cho [4] has also used the lumped parameter estimation method to calculate bulk thermal properties of a LiSOCl$_2$ cell. The problem with this theoretical estimation method for a cell is that only the manufacturer of a cell can furnish the user with information on the cell components. Most companies will not, for proprietary reasons, give out such information to their customers. Furthermore, furnishing such information to the numerous users of a commercially available cell may not be economical to the cell manufacturer. This work extends an earlier work in ref. 5 that reported measurements at 20 °C for only the BCX chemistry.

The major objective of this work is to determine experimentally the heat capacity of a Li/BCX DD-cell over a temperature range of 0 to 60 °C. These parameters are needed in the development of a realistic thermal analysis/model of the spirally-wound Li/BCX cell. The thermal model on the other hand will provide a means by which good thermal management of the system and other (NASA) projected systems can be designed, built and implemented. The objectives were achieved by determining calorimetrically the thermophysical properties of the cell at different temperatures. This work will be the first time (to our knowledge) that the effective bulk heat capacity of a Li/BCX DD-cell is estimated experimentally and compared to that of a high rate Li/SOCl$_2$ D-cell at different temperatures. The experimental results obtained will be useful in developing a thermal model for predicting the time-dependent temperature profile in a Li/BCX DD-cell. Such predictions will be helpful in the design of a thermal management system for the Li/BCX battery.

Assuming differences do exist in the heat capacities of the active and passive materials of a cell, one expects the relative amounts of these components, cell design and chemistry to impact on the bulk heat capacity of the cell. For the Li/BCX DD- and Li/SOCl$_2$ D-cells, the mass fractions of the passive parts are 0.48 and 0.52, respectively. Both cells are spirally wound. The effects of the design differences and relative amounts of passive parts may not account completely for the differences in their bulk thermal capacities.

Theory

For the determination of the bulk heat capacity, C_p, of a sample, the method of drop calorimetry is employed. This involves measuring the energy (J) gained or lost from a sample that is transferred from a bath at one temperature T_1, to one at another

temperature T_2. The energy absorbed or lost is related to the heat capacity of the sample, C_p, as

$$E_n = \int_{t_1}^{t_2} Q \, dt = \int_{T_1}^{T_2} m C_p \, dT \tag{1}$$

An integration of the area under the heat rate curve yields the total heat change from which the bulk heat capacity, C_p, can be evaluated:

$$C_p = \frac{E_n}{m(T_2 - T_1)} \tag{2}$$

where m = mass of the sample (kg), T = temperature (K), Q = heat rate (W) and t = time (s). Here, integration is interpreted as finite changes in conditions and the temperature change, $(T_2 - T_1)$ is assumed to be $\leqslant 10$ °C and C_p is constant within the temperature range.

Experimental

Li/BCX DD-cell, type 3B2085-XA and the high rate Li/SOCl$_2$ D-cell, type 6P204-ST both manufactured by Wilson Greatbatch, Ltd. (Clarence, NY, USA) were used for all the experiments. These were commercial cells manufactured to meet safety requirements of NASA. The Li/BCX cell has a capacity of 20 A h at a maximum load of 1.0 Ω at room temperature. These cylindrical cells are approximately 3.32 cm in diameter by 10.43 cm long with working electrode (anode) surface area of 372 cm^2. The Li/SOCl$_2$ D-cell is a high-rate cell capable of delivering up to 5.0 A. It has a capacity of 10 A h at a maximum current of 5.0 A at room temperature. The Li/SOCl$_2$ D-cell is 3.32 cm in diameter and 5.0 cm long with 530 cm^2 working electrode (anode) surface area.

A Hart Scientific calorimeter system, model S77XX (Hart Scientific, UT, USA) was used for all experiments. The calorimeter system designed for heat conduction calorimetry and drop calorimetry can permit standard shaped materials to be tested without immersing them in a liquid. It can accommodate samples 13.34 cm diameter by 27.94 cm tall and measure heat sources from 1.0 mW to 50 W. An aluminum cell holder was designed to conduct heat from the cell to chamber walls.

The calorimeter is based on the Seebeck or thermocouple effect. The thermoelectric sensors mounted in the chamber walls generate voltages that are proportional to the small temperature gradient between the sample side and the water bath side of the chamber walls. The voltage signal is proportional to the heat flow. Thus, by knowing the voltage generated, the amount of heat flow can be calculated. The main calorimeter water bath has an air bath above it which is set at the same temperature as the water bath to minimize temperature gradient effects between the chamber and its exterior. Further, the calorimeter baths are continuously stabilized to set temperatures within ±0.002 °C.

In addition to the calorimeter, an equilibrium bath was used for the heat capacity measurement. The equilibration bath was set at a temperature different from those of the water and air bath chambers. A higher or lower equilibration bath temperature could be used. The test item was then allowed to equilibrate for at least 8 or 10 h in the equilibration chamber. The item was transferred ('dropped') manually into the water and air bath chamber and allowed to equilibrate. The temperature probe was

also transferred from the equilibration bath water to that of the calorimeter. The total thermal capacity of the test article was related to the temperature change in the water and air bath chambers of the calorimeter.

A cylindrical aluminum 6061-T6 sample (same dimensions as a DD-cell) was used for the calibration of the system. The thermal properties and temperature dependence of the thermal properties of the aluminum sample were known. The same process of equilibration and 'dropping' used for the cells was also used for the calibration sample. A 100% copper (with dimensions of a DD-cell) was used to check the intergrity of the tests.

Results and discussion

A calibration plot for the temperature range 0 to 60 °C is presented in Fig. 1, while the intergrity or consistency test results are given in Table 1. The largest difference between the experimentally-determined heat capacity and the published values was 0.85% at 60 °C. Typical thermograms for a DD-cell at 0 and 100% depth-of-discharge
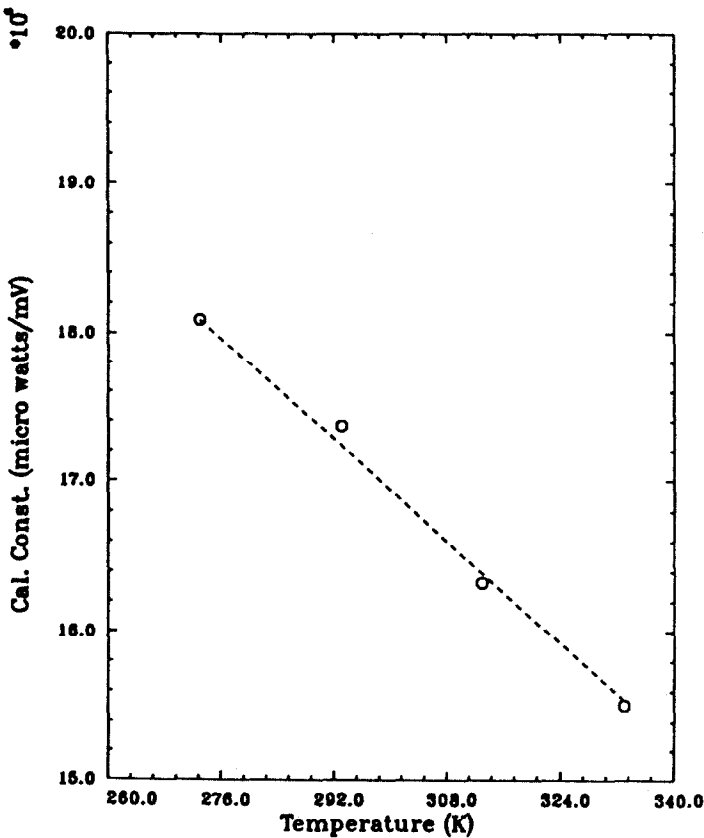

Fig. 1. A calibration plot for drop calorimetry.

TABLE 1

A comparison of experimental and published heat capacities for a standard copper sample
(shaped as a DD-cell) in J/(kg K)

Temperature (°C)	Published C_p[a] (J/(kg K))	Measured C_p (J/(kg K))	Percent difference[b]
0	384.4	382.0	0.63
20	388.5	385.6	0.76
40	388.3	385.1	0.83
60	390.2	386.9	0.85

[a]Ref. 6.
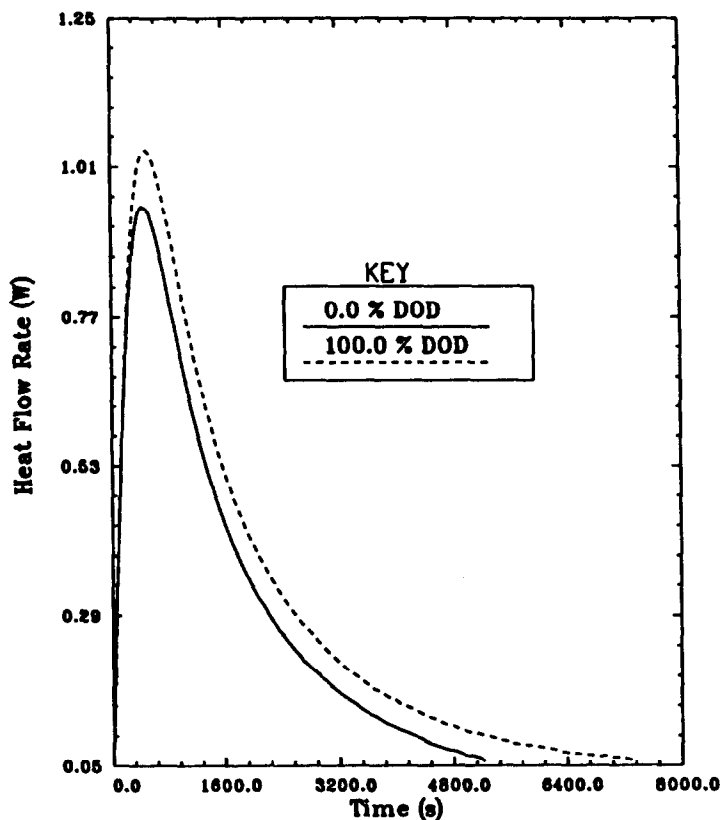[b]Percent difference = (published-experimental)/published.

Fig. 2. Thermograms of Li/BCX cell at 0 and 100% DOD at 20 °C.

(DOD) (2.0 V cut-off voltage) are shown in Fig. 2. The area under the thermogram
yielded the total energy exchange between sample and environment.

Tables 2 and 3 are compilations of data collected for the Li/SOCl$_2$ D-cells and
Li/BCX DD-cells, respectively. A check on the reproducibility of the experimental

TABLE 2

A compilation of data collected for the Li/BCX DD-cells

Temperature (°C)	Cell's serial number	Heat capacity (J/(kg K))	
		0% DOD	100% DOD[a]
0	dd3	741.28	877.87
	dd1	645.45	859.79
20	dd42	818.57	602.79
	dd44	837.16	1080.57
40	dd12	838.40	842.07
60	dd41	839.20	848.00

[a]Cut-off voltage = 2.0 V.

TABLE 3

A compilation of data collected for the Li/SOCl$_2$ D-cells

Temperature (°C)	Cell's serial number	Heat capacity (J/(kg K))	
		0% DOD	100% DOD
0	d8	820.50	847.94
	d13	796.84	
20	d10	792.08	802.06
	d11	807.18	840.08
40	d6	927.02	914.54
	d9	920.06	934.15
60	d7	861.76	882.30

results was carried out by multiple drops. Three or more repeated tests per cell per temperature yielded standard deviations from the mean of 9.38 and 9.80 J/(kg K) for the DD-cells and D-cells, respectively.

The results on the DD-cells show a C_p variation between 645.45 to 839.2 J/(kg K) (0.154 to 0.201 cal/(g °C) at 0% DOD and 602.79 to 1080.57 J/(kg K) (0.144 to 0.203 cal/(g °C) at 100% DOD. For those cells discharged at 20 °C, a variation was observed in the heat capacity values reported at 0 and 100% DOD. However, using the average of heat capacities at each temperature, a linear correlation between temperature and the heat capacities of these cells yielded a correlation coefficient of 0.948 at 0% DOD and 0.759 at 100% DOD. These correlation coefficients for the heat capacities suggest a temperature dependence exists with the Li/BCX DD-cell while at 0% DOD, but a poor dependence exists at 100% DOD. The correlation coefficient at 0% DOD suggests that there is less than 10% probability that the dependence of heat capacity on temperature occurred by chance; at 100% DOD, there is more than 10% chance that the temperature relationship occurred by chance. However, if the slight temperature dependence is discounted, average values for the heat capacities of these cells are 796.5 J/(kg K) and 853.92 J/(kg K) at 0 and 100%

DOD, respectively. Furthermore, the experimentally-determined heat capacities for each cell at 0 and 100% DOD are difficult. Except for one cell at 20 °C, the heat capacity results showed an increase between 0 and 100% DOD. This result suggests then that the electrochemical reaction within the Li/BCX cells resulted to a change in the thermal capacity of the cells. This observation could be possible if the consumption of the active materials (Li, $SOCl_2$, BrCl) of the cell produces products of reaction with higher thermal capacity. For example, consumption of Li leads to the formation of LiCl that is deposited in the carbon cathode. Such a deposition may impede flow of heat through the cell. Also, the consumption of Li removes a possible heat conduction path out of the cell. Another possibility could be that the electrochemically-formed sulfur dioxide, a gas, and other sulfuryl products will increase the thermal capacity of the cell. We can conclude from the experimental results that the products of the cell reaction result to a discharged cell with a higher thermal capacity than the fresh cell.

In Table 3, we observe that at 0% DOD, the correlation coefficient of the Li/$SOCl_2$ D-cell's heat capacity and mean value was 0.685 and 845.44 J/(kg K), respectively. Similarly at 100% DOD, the correlation coefficient of the heat capacity as a function of temperature was 0.597 with a mean value of 868.92 J/(kg K). These correlation coefficients depict a poor linear relation between heat capacity and temperature. However, like the Li/BCX DD-cell, the heat capacity of the Li/$SOCl_2$ D-cell increased from its value at 0 to 100% DOD. Overall, it was observed that the heat capacity for the D-cell varies from 792.08 to 927.02 J/(kg K) (0.191 to 0.221 cal/(g °C)) at 0% DOD and 802.06 to 934.15 J/(kg K) (0.196 to 0.223 cal/(g °C)) at 100% DOD. This suggests that the conclusion made for the Li/BCX cell as to why the heat capacity increased with the state-of-discharge could be made here for the Li/$SOCl_2$ D-cell. The results here show that the heat capacity of Li/$SOCl_2$ D-cell is higher than that of Li/BCX DD-cell.

In comparing the present results with those of Kubow et al. [3] and Takeuchi et al. [2], we observe from Table 4 that ref. 3 reported a range of 0.199 to 0.203 cal/(g °C) for the Li/BCX DD-cell while a value of 0.201 cal/(g °C) was obtained by a theoretical calculation. The results of ref. 3 contrast the present work where the range was 0.154 to 0.201 cal/(g °C) for the Li/BCX DD-cell. The heat capacity results in ref. 3 for the Li/BCX D-cell gave values that are slightly higher than those for the Li/BCX DD-cell. In a previous work by Takeuchi et al. [2], the value of heat

TABLE 4

Comparisons of heat capacities in cal/(g °C) of D-cells and DD-cells

Reference	Li/BCX DD-cell	Li/BCX D-cell	Li/$SOCl_2$ D-cell
This work			
Experimental	0.154–0.201		0.191–0.221
Calculated	0.207		0.177
Ref. 2			
Experimental		0.237–0.252	
Calculated			
Ref. 3			
Experimental	0.199–0.203	0.200–0.211	
Calculated	0.201	0.194	

capacity reported for Li/BCX D-cell varied from 0.25 to 0.56 cal/(g K). Comparing the results of ref. 3 for Li/BCX D-cell with that of Li/SOCl$_2$ D-cell obtained in this work, a negligible difference in the heat capacities of the two cells is observed.

Error Analysis

In the method used for the determination of the thermal capacities of the cells, the major sources of error include: (i) sensitivity/time delay (limitations imposed by equipment design) of calorimeter, and (ii) sample transfer method from equilibration bath to calorimeter. The response of the calorimeter to heat flow changes is normally delayed relative to the actual time the heat flow was initiated. This problem is inherent with any device used for measuring time-dependent parameter such as heat flow. A calorimeter that has a faster response time could improve on the present results but will not eliminate entirely the error associated with the system response.

The sample was physically (a holder of low (or non-) thermal conductivity used) transferred from the equilibration bath to the cell holder in the calorimeter bath. Although the time taken for the transfer to occur was negligible relative to the cooling/ heating period in the calorimeter, however, some heat loss was expected to have occurred during this short period. An appropriate method to eliminate this error would involve transferring the sample automatically without exposing it to an environment different from the equilibration bath environment before it reaches the calorimeter. In this work, it is our belief (based on results obtained for aluminum and copper samples of known thermal properties) that the errors associated with the outlined sources are negligible such that the results reported here may not be less than 98% of the exact values. At 95% confidence interval, the precision of the measurements (for the cell samples) was ±3.98%.

Conclusions

The method used in this work for the determination of the heat capacity of a cell has advantages over other methods that may involve the contact of the cell with a liquid. For the present method, the cell did not come into contact with any liquid and also the method does not involve the destruction of the cell.

This work has demonstrated that the cell's heat capacity is dependent on the state-of-charge and in most cases increases with increase in the depth-of-discharge (as the active materials of the cell are consumed in the electrochemical reaction). Furthermore, significant variation from cell to cell was observed. The only explanation is that these differences could be attributed to manufacturing variation and the cells were two years old in storage at room temperature.

We have also shown that the heat capacity of Li/SOCl$_2$ D- and Li/BCX DD-cells do depend on temperature within 0 to 60 °C. However, the dependence on temperature was shown not to be very strong. The Li/BCX DD-cell was found to have a slightly lower heat capacity than the Li/SOCl$_2$ D-cell. The results obtained here compare favorably with results reported in the literature through other methods. A comparison of the heat capacity of the Li/BCX D-cell obtained by other methods with that of Li/SOCl$_2$ D-cell from this work shows a negligible difference between the two DD-cell as observed in the work of Kubow et al. [3].

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