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at CoPP/PG electrode in 0.05M H₂SO₄ and in pH 7.9 buffer solutions are compared, shown in Fig. 10. In acidic solution these values are much larger. In both solutions the values of k , γk , γ decrease with Q value passing through the electrode. When $Q < 20$ mC, the decrease is faster, then becomes slow gradually.

Conclusion

A rapid rotation-scan method was used successfully to measure i - ω curves in the catalytic process. Very good linearity in the Koutecky-Levich plots for H₂O₂ oxidation at the CoPP/PG electrode was obtained from i - ω data. Kinetic data of k , γk , and γ were also calculated. The kinetic analysis indicated that at the beginning of catalytic reaction the electrode activity decreases faster, then becomes slower. For the decrease of electrode activity or other non-limiting current cases, the Koutecky-Levich equation can still be used to calculate kinetic parameter as long as one uses a simple corrective factor (γ). The rapid rotation-scan provided a convenient electrochemical method to study the variation of catalyst sites with time.

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Calorimetric Determination of the Thermoneutral Potential of Li/BCX and Li/SOCl₂ Cells

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ABSTRACT

Through a continuous recording of the cell voltage, heat flow, and current, the effective thermoneutral potential, E_{etp} of Li/BCX and Li/SOCl₂ cells were determined in the temperature range, 0-60°C. The depth of discharge (DOD), temperature (T), and cell type (cell chemistry) affect the effective thermoneutral potential. The effective thermoneutral potential, E_{etp} differs from the classical thermoneutral potential of a cell because it takes into account the heat flow due to non-faradaic processes. The average effective thermoneutral potential at 25°C (determined by selecting the most constant region of E_{etp} vs. time of discharge) was 4.0 and 3.84 V for BCX and Li/SOCl₂ cells, respectively. Based on the classical approach, the reversible cell potential, E_r and temperature dependence of reversible cell potential, dE_r/dT for BCX cell were 3.74 V and -0.852 mV/K, respectively, and for Li/SOCl₂, $E_r = 3.67$ V and $dE_r/dT = -0.567$ mV/K. The thermal polarization ($E_{\text{etp}} - E_1$), where E_1 is the load voltage, for both cells, showed that they are most thermally efficient near 40°C. A measure of the heat flow for both cells at 50% DOD supports this observation. An overall reaction proposed for the BCX chemistry is supported by the calculated thermodynamic parameters.

Li/BrCl in SOCl₂—known as Li/BCX cell—has an extensive history in space applications. When compared to the Li/SOCl₂ cell, Li/BCX cell exhibits such features as higher open-circuit voltage (3.90 V for the fresh cell), higher capacity, better low temperature discharge behavior, and an improved safety features.^{1,2} Its largest application to date consists of an eight D-cell battery used in the Space Shuttle. Expanding its use to large energy manned spacecraft applications will require accurate and precise determination of the cell's thermal properties. Compared to Li/SOCl₂ chemistry, very little thermal information on BCX chemistry is known.

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In spite of the well known performance differences between BCX and Li/SOCl₂ cells, the common assumption often made is that the two chemistries have identical thermal properties. The purpose of this paper is to challenge that assumption. For an effective design of thermal management system for large batteries, accurate and precise thermal properties are required. These properties can be obtained through a direct measure of the cell's heat output under discharge in a calorimeter. We will show that the absence of high voltage seen in the discharge characteristics of fresh BCX cell, because of presence of Br₂/Cl₂ constituents in the cell, may not affect the thermal behavior of the BCX cell.

The determination of the heat generation characteristics of cells by direct measurement of the heat generated during

discharge or by the determination of the thermodynamic parameters (*i.e.*, reversible cell potential, E_r , and the temperature dependence of reversible cell potential, dE_r/dT) have been carried out for many cell systems including Li/SOCl₂ cells.³⁻⁶ In addition, theoretical thermal analysis of the Li/SOCl₂ cell has also been presented.⁷⁻⁹ Unfortunately, the experimental or theoretical work in the study of the thermal behavior of Li/BCX cell chemistry is scanty.¹⁴ Further, a comparative study of the thermal characteristics of high rate Li/SOCl₂ and moderate Li/BCX cells will be useful in understanding and designing lithium-oxyhalide batteries.

The classical approach for the thermal analysis of a cell involves the comparison of expected or theoretical heat flow (calculated using thermoneutral potential, E_h , and current) against the measured heat flow. This approach, though logical does not give accurate heat flow values because it does not take into consideration the heat flow contributions made by non-faradaic processes. This work intends to show the usefulness of effective thermoneutral potential, E_{etp} , as a design tool in battery construction. E_{etp} takes into consideration all the heat flow sources during cell discharge. E_{etp} is not a universal constant since rate of discharge, cell design, material of construction, and other resistive sources may impact on the E_{etp} value.

Heat generation rates in commercial Li/BCX (DD) and high rate Li/SOCl₂ (D) cells were obtained by measuring the heat produced during cell discharge in a Hart Scientific calorimeter system. Twelve cells (6 DD-Li/BCX and 6 D-Li/SOCl₂) were discharged at five different temperatures between 0-60°C. The results were used to determine the effective thermoneutral potentials of the cells at these temperatures.

Theory

The total heat, q_t , generated during an electrochemical discharge is made up of three component parts—heat generated due to polarization, q_p , heat due to entropy effects, q_s , and heat, q_o , due to other sources other than those mentioned above. The q_p and q_s terms are expressed in terms of temperature, reversible cell potential, E_r , and its dependence on temperature.³ The total heat flow, W_t , is obtained by differentiating the sum of the three heat sources with respect to time. By neglecting the heat flow due to non-faradaic sources, q_o obtain, W_o

$$W_o = -I \left(E_r - T \frac{dE_r}{dT} - E_i \right) \quad [1]$$

The first two terms inside the parentheses of Eq. 1 are the classical thermoneutral potential. The effective thermoneutral potential, E_{etp} is defined as

$$W_t = -I(E_{etp} - E_i) \quad [2]$$

where

$$E_{etp} = E_r - T \frac{dE_r}{dT} - \frac{1}{I} \frac{dq_o}{dt} \quad [3]$$

Thus, when q_o is not included, the classical thermoneutral potential, E_h , is obtained and provides approximate heat flow from the cell. Except when the value of q_o is accurately known, direct measurement of heat evolved in a cell during discharge can only provide its effective thermoneutral potential. The difference between E_{etp} and E_h of a cell accounts for the chemical thermal power and other non-faradaic processes. It is true that q_o (in theory) could be broken down into its component parts, however, no accurate method exists for separating it from the rest of evolved heat. Partly, q_o changes with depth of discharge. Also, depending on the rate of discharge and temperature, the value of q_o may not be negligible for the Li/BCX and Li/SOCl₂ cells.

Materials

Li/BCX DD-cell, type 3B2085-XA and the high rate Li/SOCl₂ D-cell, type 6P204-ST manufactured by Wilson

Greatbatch, Ltd. (Clarence, NY) were used for all the experiments. These were cells manufactured to meet NASA requirements. The Li/BCX cell has a capacity of 20 Ah at a maximum load of 1.0 Ω at room temperature (25°C). These cylindrical cells are approximately 3.32 cm diam by 10.43 cm long with working electrode (anode) area of 372 cm². The Li/SOCl₂ D-cell is a high rate cell capable of delivering up to 10 Ah at a maximum current of 5.0 A at room temperature. The Li/SOCl₂ D-cell has a 3.32 cm diam and 5.80 cm long with 530 cm² working electrode (anode) surface area.

Equipment

A Hart scientific calorimeter system, Model S77XX, was used for the 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 diam 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 the chamber walls.

The calorimeter is based on 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. 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. A Kepco (New York) series BOP 36-12M (Model 195A) bipolar power supply, rated for a maximum power output of 400 W and capable of voltage or current control was used for all the experiments.

Methods

To determine the rate of heat release under load, a No. 20 AWG wire was soldered to both the anode and cathode tabs of the cell. The cell was fitted into the sample chamber of the aluminum cell holder with the wires connected to copper segments which were connected to the power supply. The copper segments heat sinked the leads going and leaving the cells to minimize wire heat losses from the chamber to the exterior. This arrangement was calibrated with a precision resistor (to 1.0%) as the known heat source. The resistor was powered and configured in a manner identical to the cell conditions. This method allowed the calibration of all heat losses and was performed at every temperature tested. A known heat source was put in, $q_{in} = q_{out}$. The calibration results are shown in Fig. 1.

Each cell was kept in this constant temperature chamber to equilibrate for at least 8 h before any measurements were made. The calorimeter system was controlled by a Dell computer and a second similar computer system was used for the acquisition of data. The data was stored on disk for subsequent plotting and analysis. The data acquisition system monitored the cell current (Keithley multimeter was used), the voltage, and temperature (microtherm 1701 used). Discharges were conducted at four different temperatures between 0-60°C.

Results

Through a direct measurement of heat evolved on discharge in a calorimeter, the effective thermoneutral potentials of Li/BCX and Li/SOCl₂ cells were determined. From the heat flow, cell voltage and current measurements, the E_{etp} of each cell from 0-100% DOD was calculated using rearranged form of Eq. 2. Figures 2 and 3 show, respectively, the typical results obtained for the Li/BCX and Li/SOCl₂ chemistries. In the figures, the load voltage (E_l), effective thermoneutral potential (E_{etp}), and the heat generated (W) on discharge are presented as functions of capacity. The results could be interpreted in terms of discharge time in hours. Figure 4 compares the E_{etp} of the BCX and Li/SOCl₂ cell chemistries as functions of temperature. The dependence of the BCX and Li/SOCl₂ cells' polariza-

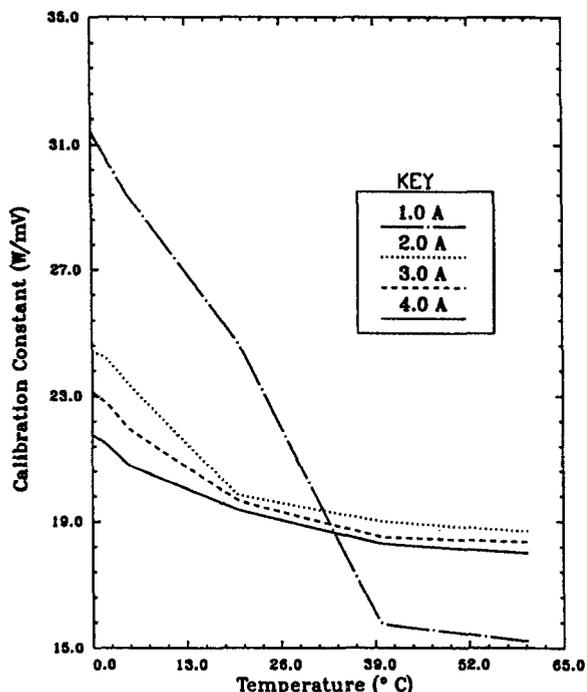


Fig. 1. Heat conduction calibration results at different currents.

tions [defined as the departure of the load voltage from the effective thermoneutral potential, $(E_{etp} - E_l)$] on temperature is shown in Fig. 5.

Discussion

To meet part of the objectives of this work, the determination of the E_{etp} of both Li/BCX and Li/SOCl₂ was used to characterize both cells. Unlike the thermoneutral potential, E_h of a cell which represents only the enthalpic portion of the open-circuit potential (purely a thermodynamic parameter) i.e.

$$E_h = -\frac{\Delta H_r}{zF} = \frac{-\Delta G_r - T\Delta S_r}{zF} = E_r - T \frac{\partial E_r}{\partial T} \quad [4]$$

the effective thermoneutral potential E_{etp} includes the potential due to other reactions which can contribute and

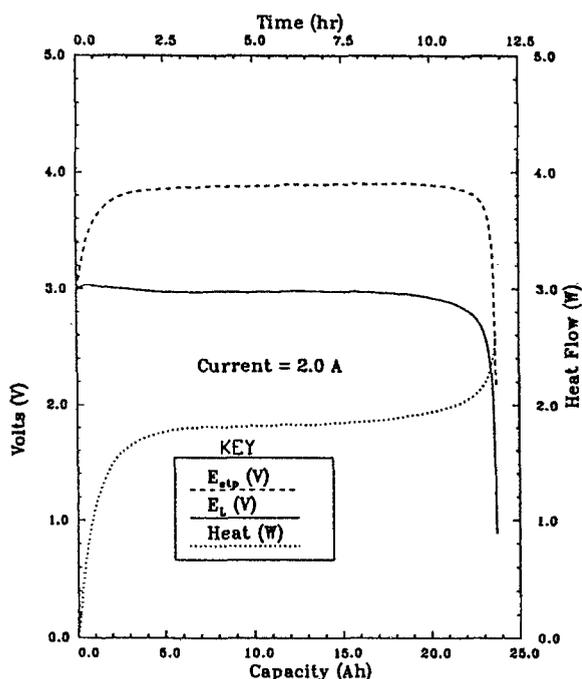


Fig. 2. Effective thermoneutral potential, load voltage, and rate of heat generation for a Li/BCX cell at 20°C.

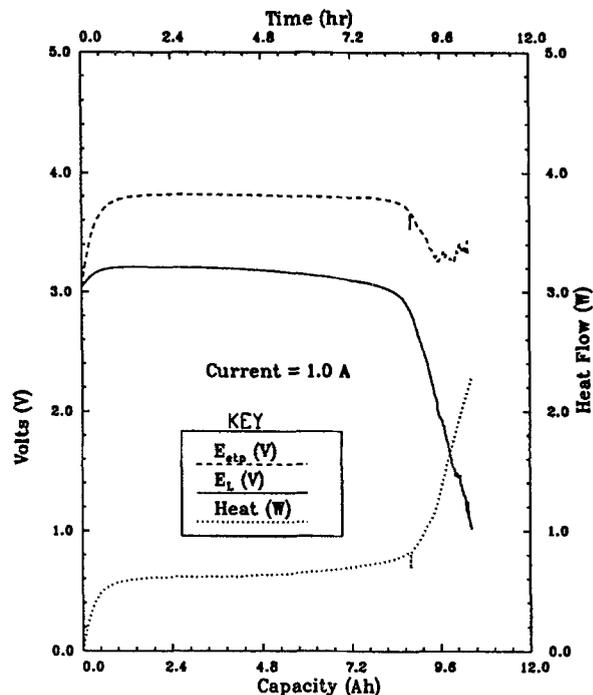


Fig. 3. Effective thermoneutral potential, load voltage, and rate of heat generation for a Li/SOCl₂ cell at 20°C.

affect the heat values such as corrosion reactions and resistive loads (combination of thermodynamics and kinetics). Though the calculation of heat flow in a cell based on the

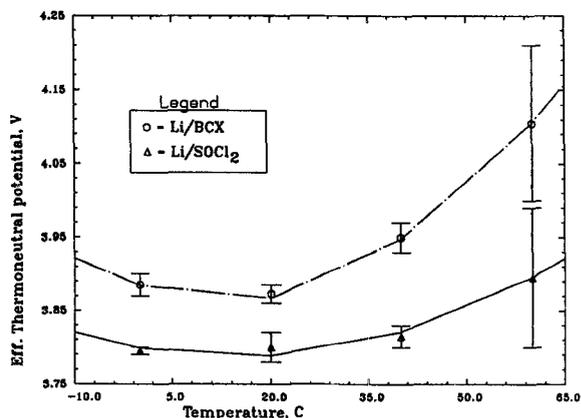


Fig. 4. A comparison of the effective thermoneutral potential as a function of temperature for Li/BCX (5.37 mA/cm²) and Li/SOCl₂ (1.89 mA/cm²) chemistries.

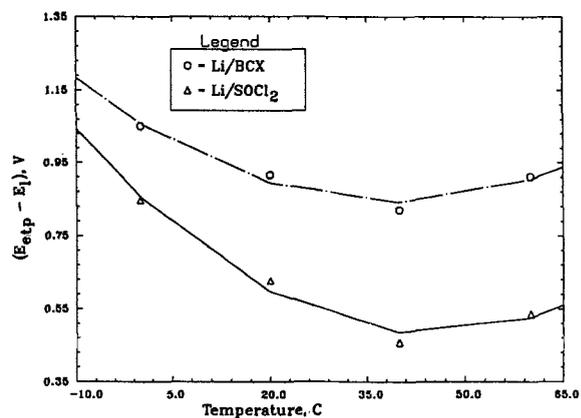


Fig. 5. Polarization vs. temperature for Li/BCX (5.37 mA/cm²) and Li/SOCl₂ (5.37 mA/cm²) chemistries.

use of E_h should produce logical values, however, this is not the case in practice because E_h accounts only for the primary electrochemical reactions. Thus, the E_{etp} should be of more interest to the battery engineer since the interest of the engineer is concerned with the total heat produced by the cell under discharge rather than separation of the heat producing processes into different components.

Both the Li/BCX and Li/SOCl₂ cells exhibited a flat discharge curve with little or no apparent voltage delay at all the temperatures. This could be due to the fact that both cells were about a year old from the date of manufacture. The absence of the hump (related to the presence of BrCl) normally found in the voltage curve of a fresh BCX cell does not seem to be critical in the total thermal output of the cell. Figures 2 and 3 show the dependence of the E_{etp} on the depth of discharge (DOD). For both chemistries, the E_{etp} initially rose with DOD until a certain value at which it remained nearly constant for most of the discharge duration. Towards the end of discharge, when the active materials have been apparently exhausted, the effective thermoneutral potential then decreased very rapidly. The heat flow showed a behavior similar to the E_{etp} at the inception of discharge and for most of the discharge duration; however, towards the end of discharge, the heat flow increased very rapidly while the E_{etp} decreased.

In Fig. 4, the average E_{etp} is plotted as a function of temperature. The figure shows that E_{etp} for both cells was sensitive to temperature. Figure 4 shows that the E_{etp} for the BCX cell is higher than that of Li/SOCl₂ cell in the temperature range 0–60°C. At the 0–60°C range of experiment, the minimum effective thermoneutral potential occurred near 20°C for both cells. Figure 5 shows a temperature dependence of the cells' polarizations, with minimum polarization value in the neighborhood of 40°C for both chemistries. This observation implies that both cells are most thermally efficient near 40°C. Thus, minimum heat generation is expected near 40°C since the cell's polarization is proportional to the heat generation rate. This observation is confirmed by Fig. 6, which shows a plot of heat generation rate in both cells at 50% DOD as a function of temperature. Minimum heat was generated near 40°C for both cell chemistries. The minimum amount of heat generated near 40°C amounted to 7.824 and 3.833 mW/g by the BCX and Li/SOCl₂ cells, respectively. The higher amount of heat generation in BCX is as predicted by its higher effective thermoneutral potential. Although both cells were not discharged at the same rate, it is apparent from the effective thermoneutral potentials of both cell chemistries, that their thermal characteristics are different. This contrasts with the common assumption often made. It is commonly assumed that after the BCX cell passes the high voltage hump in its discharge curve (a characteristic attributable to the presence of BrCl), its behavior becomes similar to that of the Li/SOCl₂ cell. Our result here indicates that even in the absence of the voltage hump, the thermal character-

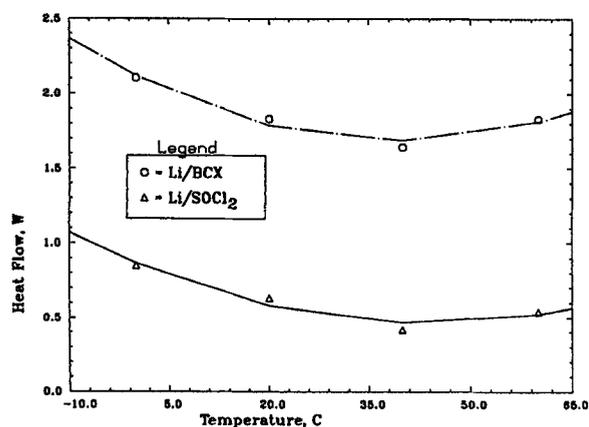


Fig. 6. Temperature dependence of heat flow in Li/BCX (5.37 mA/cm²) and Li/SOCl₂ (5.37 mA/cm²) cells at 50% DOD.

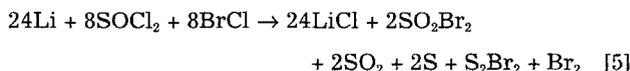
istics of the BCX chemistry are different from those of Li/SOCl₂ chemistry.

The cell's open circuit potential was assumed to be the same as the reversible cell potential. This is a valid assumption as long as there are no impurities on the electrode surface, *i.e.*, pure and very clean electrode surface. Assuming a negligible faradaic process, and with the temperature of experiments known, the E_{etp} was used to estimate the temperature dependence of the reversible cell potential at different temperatures. This is the classical thermoneutral potential approach. The average of these values yielded -0.852 and -0.567 mV/K for BCX and Li/SOCl₂ cells, respectively. Using these values, the estimated thermal voltages for both cells at 25°C are 3.84 and 3.98 (≈ 4.0) V for Li/SOCl₂ and BCX cells, respectively. This result for Li/SOCl₂ cell compares favorably with both theory and literature values for the thermoneutral potential.^{3,6} This shows that previously determined thermoneutral potential values in the literature for Li/SOCl₂ cell were really the effective thermoneutral potential since the effects due to non-faradaic processes were not separated. The close agreement between the values obtained through cell discharge and thermodynamic measurement is explained as due to the low discharge conditions normally employed for such experiments. Under a very low discharge condition, the thermal effects due to non-faradaic processes are small.

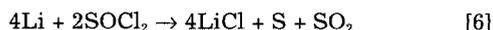
We are not aware of data in the open literature on the effective thermoneutral potential of Li/BCX cell; however, Godshall and Driscoll³ and more recently Bittner *et al.*,⁶ have reviewed the classical thermoneutral potential data for the Li/SOCl₂ cell. Using the E_{etp} obtained in this work as the classical E_h , a comparison is made in Table I between the present results and those obtained in the literature by calorimetry for Li/SOCl₂ cell. The close agreements between the thermal potential values support our view that these values are the effective thermoneutral potentials of the cells. The slight differences may be partly accounted for as due to differences between discharge rate and cell design differences.

The difference between the E_{etp} of Li/BCX and Li/SOCl₂ cells suggests less heat generation in Li/SOCl₂ cells under the same load and operating conditions. Thus, the presence of BrCl in thionyl chloride seems to improve the cell's operating voltage at the expense of more heat generation. BrCl in BCX cell modifies some of the discharge products associated with Li/SOCl₂ chemistry and the surfaces of the electrodes. The results here suggest that BrCl and the modified discharge products of Li/SOCl₂ chemistry affect the polarization process in Li/BCX or result in a controlled process such that more heat would be generated in Li/BCX cell than in a Li/SOCl₂ cell under the same discharge conditions.

Abraham *et al.*¹⁰ suggested a mechanism for the Li/BCX cell discharge. According to this mechanism, the dissociation of BrCl is followed by a step wise reduction of BrCl via Cl₂, Br₂ and BrCl as shown in Eq. 2 through 5 of Ref. 10. A reaction between LiBr and SOCl₂, as given in Eq. 9 of Ref. 10, is followed by the main electrochemical reduction of SOCl₂. If we assume that Eq. 9 and 11 of Ref. 10 are the reaction products of Li/BCX cell discharge, then the overall expression for the cell reaction in Li/BCX cell could be given as



The accepted overall cell reaction for the Li/SOCl₂ is similarly expressed as



If the chemical reaction within the cell was known, the classical thermoneutral potential can be calculated independently of the calorimetric data obtained in this work. For instance, if the differences between standard states and the actual cell conditions are neglected, the above equation for Li/SOCl₂ cell reaction yields a $\Delta H = -366$ kJ/eq. and $E_h =$

Table I. Thermodynamic parameters of lithium thionyl chloride cell by calorimetry at 25°C.

Ref.	ΔH (kcal/eq.)	E_h (V)	ΔS (cal/K-eq.)	dE_r/dT (mV/K)	ΔG (kcal/eq.)	E_r (V)
4	-90.4	3.92	-11.3	-0.46	-83.9	3.65
12	-87.6	3.80	-20.8	-0.90	-81.4	3.53
3	-87.4	3.783	-7.74	-0.33	-83.9	3.65
13	-89.44	3.877	-17.93	-0.777	-84.1	3.65
This work	-88.59	3.84	-13.08	-0.567	-84.69	3.67

3.793 V at 25°C. Neglecting the thermal effects due to non-faradaic process in BCX discharge, the E_{etp} obtained in this work (4.0 V) is equivalent to an overall reaction of $\Delta H = -92.30$ kcal/eq. and a value of -0.852 mV/K for dE_r/dT or an entropy change (ΔS) of -19.6 cal/K-eq. From these values, the free energy change, ΔG of the BCX cell reaction is -86.44 kcal/eq. and $E_r = 3.746$ at 25°C. Using data from Ref. 11, the thermodynamic parameters calculated for reaction 11 were: $\Delta H(298) = -93.53$ kcal/eq., $\Delta G(298) = -88.92$ kcal/eq., and $\Delta S(298) = -15.5$ cal/eq. Based on these values, we obtain theoretically, $E_h = 4.05$ V, $dE_r/dT = -0.672$ mV/K, and $E_r = 3.85$ V (at 25°C) for Li/BCX cell. It must be borne in mind that the theoretical values calculated are estimates which are likely to be higher than exact values, since standard conditions were assumed for the species in the electrolyte solution. However, the close agreement between the theoretical E_h and the experimentally determined E_{etp} is an indication that the proposed overall cell reaction for BCX chemistry could be correct. The experimental results obtained here show that both Li/BCX and Li/SOCl₂ cells will operate most thermally efficient near 40°C.

Error Analysis of Experimental Results

The sources of error in the calorimetric measurement include the calorimeter, impurities in the cell's solvent system, corrosion, and chemical reactions. Most of these sources of inaccuracies cannot be eliminated. For instance, the reversible cell potential of a cell is a function of solvent purity in contact with the electrode. Since commercial cells were used (which may contain proprietary additives), there was not a way of eliminating this source of inaccuracy. Furthermore, the response or characteristic time and accuracy of the calorimeter to measure heat flow is dynamically related to the system design. The response or characteristic time of the calorimeter was the reason why the 2.0 and 1.0 A discharge rates were chosen for the Li/BCX and Li/SOCl₂ cells, respectively. By choosing the rates used here, the depth of discharge of the cells was low when the calorimeter system stabilized to its steady state. The effective thermoneutral potential measured for both Li/BCX and Li/SOCl₂ chemistries showed a $\pm 0.8\%$ reproducibility at 20°C. The E_{etp} test results were extrapolated to 25°C with a standard deviation of 0.126 and 0.063 V, respectively, for Li/BCX and Li/SOCl₂ cells. The higher standard deviation obtained for the BCX chemistry suggests that BrCl does introduce a higher variability in the thermodynamic parameters of the BCX when compared to Li/SOCl₂ cell. A

1.0% precision resistor used for calibration showed that input heat was equal to output heat and thus an accuracy within $\pm 1.0\%$ was achieved with the system.

Conclusion

The effective thermoneutral potential obtained for the Li/BCX cell ($E_{\text{etp}} = 4.0$ V) was greater than the measured reversible or open-circuit potential ($E_r = 3.74$ V). Similar observations were made for the Li/SOCl₂ chemistry. A comparison of the heat generation at 50% DOD from both cells (though discharged at different rates) showed that the BCX chemistry generated more heat. The polarization curves and the heat rate at 50% DOD showed that both cells will be most thermally efficient near 40°C, while minimum effective thermoneutral potential for both cells occurred near 20°C.

The close agreement between the theoretically estimated thermoneutral potential (E_h) of Li/BCX and the experimentally determined E_{etp} suggests that the overall reaction proposed for the BCX chemistry could be correct. Further, it shows that the thermal effects due to non-faradaic processes may be negligible at low discharge rates such that the difference between E_h and E_{etp} may be negligible. The results obtained for Li/SOCl₂ chemistry compares favorably well with literature values and thus substantiates this work.

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