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Measurements of the Fundamental Thermodynamic Parameters of Li/BCX and Li/SOCl₂ Cells

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Measurements of the Fundamental Thermodynamic Parameters of Li/BCX and Li/SOCl₂ Cells

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ABSTRACT

The thermodynamic data needed to estimate the heat generation characteristics of Li/BCX and Li/SOCl₂ cells were determined using two experimental techniques, equilibrium or reversible cell discharge and measurement of open circuit potential as a function of temperature. The results obtained showed that the reversible cell potential (E_r), the temperature dependence of the reversible cell potential (dE_r/dT) and thermoneutral potential (E_n) of the BCX cell were respectively, $E_{r,250C} = 3.74$ V, $dE_r/dT = -0.857 \pm 0.198$ mV/K and $E_n = 3.994 \pm 0.0603$ V. The respective values obtained for the Li/SOCl₂ cell were $E_{r,250C} = 3.67$ V, $dE_r/dT = -0.776 \pm 0.255$ mV/K and $E_n = 3.893 \pm 0.0776$ V. The difference between thermoneutral potential of Li/BCX and Li/SOCl₂ cells is attributable to the difference in their electroactive components.

Li/BCX cells have flown on Space Shuttle missions on various applications since 1982. Thus far, the largest Li/BCX battery used by NASA contains eight cells. The proliferation of these cells into much larger energy batteries for future spacecraft applications requires accurate and precise characterization of cells' thermal properties to enable effective thermal management systems. Good thermal

management system ensures both proper operation and maximization of cell performance.

Measurement of fundamental thermodynamic parameters is an approach often used to determine the heat characteristics of an electrochemical cell. If the absorbed or evolved heat attributable to non-faradaic processes is negligible, then measuring the fundamental thermodynamic parameters such as the reversible cell potential (E_r) and temperature dependence of the reversible cell potential (dE_r/dT) at various temperatures provides a method of de-

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termining a cell's thermoneutral potential (E_h). The thermoneutral potential of a cell is an important estimate of its thermal capability. A cell operating at its thermoneutral potential is said to be at a thermal equilibrium in which it neither absorbs nor gives out heat during discharge. It is thus, a parameter of importance for estimating heat generation in a cell during discharge provided non-faradaic processes are negligible.

In most measurements of reversible cell potential, E_r it is assumed that the open circuit potential, E_{ocv} is the same as E_r . However, the extrapolation of the load potential at small over-potentials to zero current may be more indicative of E_r , as pointed out by Bittner *et al.*⁴ This is because the open circuit potential can be influenced by impurities (solution component activities) and surface conditions of the electrodes, while the extrapolated load potential at small overpotential is the potential of the reaction of interest and thus may be more indicative of the true equilibrium potential.

This work differs from our previous communication in which the concept of the effective thermoneutral potential was used to analyze the thermal behavior of Li/BCX and Li/SOCl₂ cells.¹ Effective thermoneutral potential differs from the cell's ordinary or classical thermoneutral potential by an amount that is attributable to non-faradaic processes occurring during cell discharge. Consequently, the thermal potential obtained by the discharge of a cell is essentially equivalent to the effective thermoneutral potential. The difference between the effective thermoneutral potential and the ordinary or classical thermoneutral potential (*i.e.*, with non-faradaic process potential excluded) is so small that it is often ignored; however, in consideration of high discharge rates and temperatures, and for the design of a very large battery, it is necessary not to overlook this difference. The relevance of this work is both to present thermal data on Li/BCX and compare with Li/SOCl₂ cells without resorting to calorimetric discharge. The usefulness of the information will be explained.

Theory

The basis of the load potential extrapolation to zero current lies in the Butler-Volmer equation

$$i = i_0 \left\{ \exp \left(\alpha_a n \frac{F\eta}{RT} \right) - \exp \left(-\alpha_c n \frac{F\eta}{RT} \right) \right\} \quad [1]$$

Here, i_0 is the exchange current density, $\alpha_{a,c}$ is the transfer coefficient (a-anode, c-cathode), n the number of electrons transferred, F the Faraday constant, R the gas constant, T the temperature, and η the overpotential. For an irreversible system such as Li/SOCl₂, α_a is very small and could be neglected. At sufficiently small overpotential, corresponding to $\eta F < RT$, by expanding the exponential terms in Eq. 1 we obtain

$$i = i_0(\alpha_a + \alpha_c) \frac{nF\eta}{RT} \quad [2]$$

In terms of the overpotential, *i.e.*, $\eta = E_l - E_r$, Eq. 2 can be rearranged as

$$E_l = E_r + \frac{RT}{i_0(\alpha_a + \alpha_c)nF} i \quad [3]$$

where E_l is the load voltage. Equation 3 indicates that a plot of E_l against i will yield a linear plot whose intercept on the vertical axis is the equilibrium (at zero current) or reversible cell potential, E_r . Once the equilibrium potential is obtained at different temperatures, then dE_r/dT can be calculated by a plot of E_r against temperature, T . The thermoneutral potential, E_h defined as the potential at which thermal equilibrium exists (*i.e.*, heat is neither absorbed nor generated) is obtained by

$$E_h = E_r - T \frac{dE_r}{dT} \quad [4]$$

Equation 4 arises from the relationship between the free energy, enthalpy, and entropy changes of an electrochemical couple.

$$\Delta G = \Delta H - T\Delta S \quad [5]$$

Substitute into Eq. 5 using $G = -zFE_r$, $H = zFE_h$, and $S = zFdE_r/dT$, and after rearrangement, Eq. 4 is obtained. Alternatively, a plot of E_r against T and its extrapolation to the vertical axis yields E_h and a gradient that is equal to dE_r/dT .

On the open circuit voltage approach, the measured open circuit potential at different temperatures is plotted as a function of temperature. The E_h and dE_r/dT are obtained from such a plot.

Experimental

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. The cells were designed to NASA's specifications. At room temperature conditions (25°C) and at a maximum load of 1.0 Ω , the Li/BCX DD-cell used has a capacity of 20 Ah while the Li/SOCl₂ D-cell has a capacity of 10 Ah at a rate of 5.0 A. Both cells are cylindrical in shape and measure approximately 3.32 cm in diam. The DD-cell is 10.43 cm long and has a working electrode (anode) surface area of 372 cm² while the D-cell is 5.80 cm long with an anode surface area of 530 cm². Water baths continuously stabilized to within $\pm 0.002^\circ\text{C}$ were used. Cells were not in contact with water.

A Kepco (New York, USA) series BOP 36-12M (Model 195A) bipolar power supply rated for a maximum power output of 400 W was operated under voltage control for the equilibrium discharge experiments. The power supply has output ranges of ± 36 V and ± 12 A. Under load control, the maximum output variations of the power supply over an 8 h period (8 h drift) is less than $\pm 0.005\%$ of its maximum rating, which is equivalent to less than 1.6 mV offset for a 10°C temperature change.

For the equilibrium discharge, a No. 20 AWG wire was soldered to both the anode and cathode tabs of the cell. The cell was then fitted into the sample chamber of the aluminum cell holder with the wires connected to copper segments which were connected to the power supply. At a given temperature, the cell was equilibrated for 3 h in the calorimeter chamber. The BOP power supply, acting as a potentiostat was set to control the cell voltage. The voltage was stepped down 5 mV and both the current and load voltage recorded (data acquisition by a computer) for another 3 h. This stepping down of voltage was carried on until 35-50 mV from the open circuit voltage had been stepped-off.

In the open circuit potential approach, the open circuit potential of BCX and Li/SOCl₂ cells were measured at four different temperatures between 0-60°C. One cell of each type was used at each temperature. The cell was kept in the constant temperature bath and the electrical leads connected similar to those for equilibrium discharge method. After 8 h of equilibration, the voltage recorded was taken as the open circuit potential.

Results and Discussion

At the end of the equilibration period (for the reversible or equilibrium discharge method), the cell voltage was stepped down from the open circuit value by 5 mV increments. The current, load voltage and time were measured or recorded. At each temperature condition, the measured cell voltage was plotted as a function of current and by a linear fit the equilibrium potential (at zero current) was obtained by extrapolation. A typical linear fit result for the BCX cell is shown in Fig. 1. The equilibrium voltage obtained at each temperature through this approach was plotted as a function of temperature as shown in Fig. 2 for both the BCX and Li/SOCl₂ cells.

The completion of the equilibrium discharge experiments took about five days for each cell. The thermoneutral potential obtained for the BCX cell showed that the use of the first two points (at two different temperatures) obtained within the first 48 h of the start of the experiment (taken before the other points) were in agreement with the values of thermoneutral potential obtained by other meth-

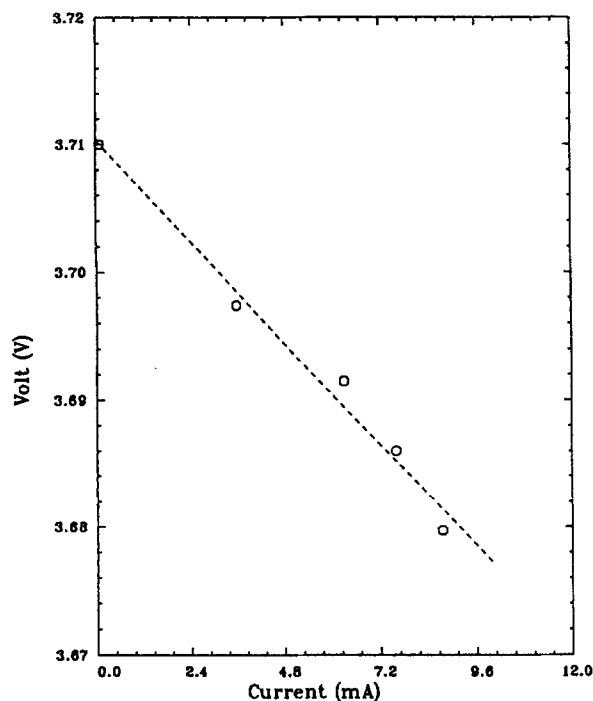


Fig. 1. Linear fit of current vs. voltage for BCX cell at 30°C.

ods.² The most probable reason for this could be attributed to either the discharge of the cell above the low current region (where Eq. 3 is applicable) or due to the adverse effects of intermediate products on the storability of BCX cell after a partial discharge.⁸ The first case was discounted since effort was made in the course of the experiments to discharge the cell within the region where Eq. 3 is applicable. A further discussion on this is provided in Ref. 2.

A plot of the equilibrium voltages at 30 and 40°C for the BCX cell as shown in Fig. 2 yielded $dE_r/dT = 1.0 \text{ mV/K}$, $E_h = 4.04 \text{ V}$ and $E_{r,350\text{C}} = 3.71 \text{ V}$. This result for the BCX cell has a 50% confidence interval of $E_h = 4.04 \pm 0.144 \text{ V}$ and $dE_r/dT = -1.0 \pm 0.467 \text{ mV/K}$. The result obtained for the Li/SOCl₂ cell, shown in Fig. 2 yielded a $dE_r/dT = -0.631 \text{ mV/K}$, $E_h = 3.86 \text{ V}$ and $E_{r,250\text{C}} = 3.672 \text{ V}$. With only a 50% confidence, the thermoneutral potential obtained for Li/SOCl₂ is equivalent to $E_h = 3.86 \pm 0.042 \text{ V}$ and similarly $dE_r/dT = -0.631 \pm 0.1406 \text{ mV/K}$.

The results obtained by the open circuit voltage (OCV) approach are plotted as a function of temperature in Fig. 3 for both the BCX and Li/SOCl₂ cells. A linear fit of the points for the BCX cell yielded $dE_r/dT = -0.857 \text{ mV/K}$ and $E_{r,250\text{C}} = 3.739 \text{ V}$. Extrapolation of the curve to absolute zero gave a value of $E_h = 3.994 \text{ V}$. For the Li/COCl₂ cell, $dE_r/dT = -0.766 \text{ mV/K}$, $E_{r,250\text{C}} = 3.665 \text{ V}$ and $E_h = 3.893 \text{ V}$. The

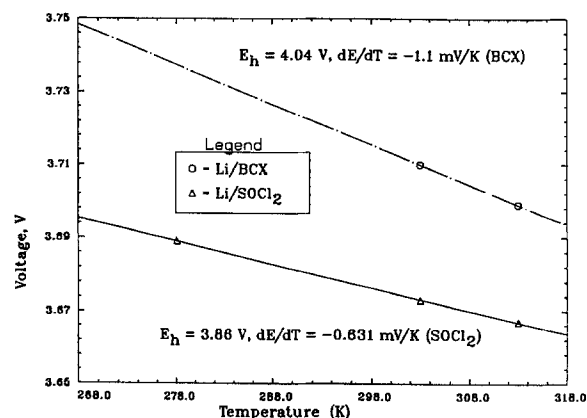


Fig. 2. Dependence of reversible cell potential on temperature for Li/SOCl₂ and Li/BCX cells (equil. discharge method).

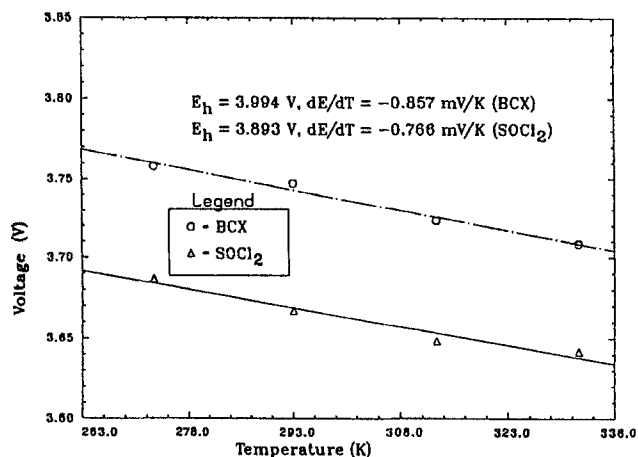


Fig. 3. Open circuit potential vs. temperature, for Li/SOCl₂ and Li/BCX cells.

results obtained through open circuit voltage approach at 95% confidence intervals is respectively equal to $E_h = 3.994 \pm 0.0603 \text{ V}$, $dE_r/dT = -0.857 \pm 0.198 \text{ mV/K}$ for BCX cell and $E_h = 3.893 \pm 0.0776 \text{ V}$, $dE_r/dT = -0.766 \pm 0.256 \text{ mV/K}$ for Li/SOCl₂ cell.

Comparing results obtained through the two methods, it is observed that the results at 50% confidence level straddle those at 95% confidence level for both cells. Thus, with its lower risk of being wrong 5% of the times, the results obtained by the OCV approach could be taken to be more reliable. Thus the ranges at which the thermoneutral potentials of BCX and Li/SOCl₂ cells lie could respectively be given as $E_h = 3.994 \pm 0.0603 \text{ V}$ and $E_h = 3.893 \pm 0.0776 \text{ V}$. Except for the work reported in Ref. 1 and 2 on the effective thermoneutral potential of BCX cell ($E_{\text{etp}} = 4.0 \text{ V}$), there is not much thermal data in the literature to compare with the thermodynamic values obtained in this work. In the case of Li/SOCl₂ cell, the thermodynamic value obtained in this work are compared with values obtained from other works in Table I. There is excellent agreement between the results from the present work and with those reported in Table I. The results from the work of Chenebault *et al.*⁵ predicted a value of dE_r/dT that is higher than any previously reported in the literature (Table I), however the effective thermoneutral potential (thermal potential, $E_{\text{etp}} = 3.884 \text{ V}$) they obtained at 40°C and a discharge rate of 1.0 mA/cm^2 is closer to the thermoneutral potential obtained in this work. As a result of the high dE_r/dT value obtained by Chenebault *et al.*,⁵ the reversible cell potential, E_r , predicted at 25°C (using their data) is quite in disagreement with both the literature values and this work. The results from the present work predict that the BCX and Li/SOCl₂ cells will both be exothermic at all load voltages (open circuit voltages are below E_h in each case) with the BCX cell being capable of more heat generation (a consequence of its higher E_h).

Conclusions

The measured parameters, E_r , dE_r/dT , and E_h are significant in the estimation of expected heat flow from a cell during discharge provided the cell voltage and discharge current are known. This is so when the current flow through the cell (dependent on a number of factors) is small and certain non-faradaic processes and electrode tab resistances do not give rise to significant heat output. However, as the current increases and polarization becomes larger, the dependence of the non-faradaic processes on the concentration of certain species in the electrolyte may result to a current dependence of the heat generated by such non-faradaic process. Consequently, the present parameters can only be used for estimation of the heat flow in a cell.

The present results thus indicate that the method of reversible cell discharge or OCV method can provide a means of predicting heat generation rates in cells without using a

Table I. Measured fundamental thermodynamic parameters of Li/SOCl₂ cell by dE_r/dT method.

Ref.	ΔH (kcal/eq)	E_h (V)	ΔS (cal/K-eq)	dE_r/dT (mV/K)	ΔG (kcal/eq)	E_r (V)
7	-89.28	3.87	-14.07	-0.61	-85.11	3.65
3	-85.82	3.72	-5.26	-0.228	-84.2	3.65
6	-77.0	3.339	23.7	1.026	-84.1	3.65
5	-86.32	3.743	-25.37	-1.10	-78.76	3.42
This work (ocv method)	-89.81	3.89	-17.67	-0.766	-84.55	3.67
(equil. meth.)	-89.01	3.86	-14.55	-0.631	-84.63	3.67

calorimeter. The thermoneutral potential, E_h obtained can be used to calculate the theoretical heat flow in a cell by multiplying the voltage difference between the discharge voltage and E_h by the discharge current, *i.e.*

$$d(-Q)/dt = I[E_r - E_l - TdE_r/dT] - H_1v_1 \quad [6]$$

where the last term is assumed negligible.

Such a heat flow obtained is approximate because it neglects the heat contributions from non-faradaic reactions and resistive heat from electrode connections. The close agreement of the results on BCX cell in this work with the result obtained by calorimetry in Ref. 1 suggests that at low discharge rates the heat due to non-faradaic processes may not be critical in predicting the heat generation in BCX cells. The agreement of the results on Li/SOCl₂ cell with literature values substantiates the work. The different thermal characteristics of the BCX cell ($E_h = 3.994 \pm 0.0603$ V) from those of Li/SOCl₂ cell ($E_h = 3.893 \pm 0.0776$ V) could partly be attributed to the slight differences in their active components. This difference puts to question the

common assumption often made about the similarity in the thermal behavior of both cell types.

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Direct Synthesis of Phenol from Benzene during O₂-H₂ Fuel Cell Reactions

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ABSTRACT

Partial oxidation of benzene to phenol at the cathode was demonstrated at room temperature during O₂-H₂ fuel cell reactions. The best cathode for this reaction was explored. Graphite, carbon black, active carbon, and carbon whisker were examined as the cathodes. Pretreatment of these carbon materials with HNO₃ aqueous solution (6.7M) at 373 K improved the rate of phenol production remarkably. Among these carbon materials, the carbon whisker showed the best results. Hydroxyl radical was suggested to be the active oxygen species responsible for hydroxylation of benzene. The reaction mechanism assuming hydroxyhexadienyl radical as a reaction intermediate has been proposed. Coaddition of Pd black and Fe-cation to the carbons showed a marked synergism for the formation of phenol. Pd black increases the rate of reduction of dioxygen. Fe-cation enhances the generation of hydroxyl radical as well as the selectivity to phenol. The combination of these effects explains the synergism of Pd black and Fe-cation. The same reaction system and the best cathode described above have been applied to the partial oxidations of toluene and cyclohexane.

The Cumene Process for the synthesis of phenol, one of the most sophisticated process currently operated in the chemical industry, requires multi-step operations throughout the whole process for converting benzene to phenol. Decreasing demand of acetone, the final by-product in the process, might cause a serious drawback of this process in the future. Thus there is a strong demand to convert benzene to phenol in one-step as an alternative to the Cumene Process, which stimulated a number of research works so far.¹⁻⁷

Recently, we have proposed a new method for direct synthesis of phenol by applying an O₂-H₂ fuel cell reaction under ambient conditions.⁸⁻¹⁰ The principle of this method is schematically shown in Fig. 1. We have suggested that the hydroxylation of benzene is initiated by an active oxygen, O*, which is generated on the metal cation in the cathode during reduction of dioxygen under short-circuit

conditions. The advantages of this method are: (i) The method does not use expensive reductant such as ascorbic acid, NADPH, NaBH₄ or zinc powder which was required for the activation of dioxygen in monooxygenase mimic systems;^{2,6,7,11,12} (ii) Since oxygen and hydrogen are separated by a proton-conducting membrane, danger of explosion is reduced; (iii) The reaction cogenerates phenol and electricity. However, the rate of phenol formation observed so far was very slow. The maximum rates of phenol formation for the iron- and samarium-embedded cathodes were 0.26 and 0.55 $\mu\text{mol} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$, respectively.⁹⁻¹⁰ Therefore, the object of this work is to improve the rate of phenol formation by modifying the cathode. The most favorable carbon material, effect of oxidation treatment of the carbons and promoting effect of metal blacks and metal salts added to the cathode will be investigated to improve the formation rate of phenol. The best cathode for the phenol formation will