COMPUTER SIMULATION OF THERMAL MODELING OF PRIMARY LITHIUM CELLS

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Summary

The objective of this program was to gain a better understanding of the safety problems of primary Li–$SOCl_2$ and Li–SO_2 cells by carrying out detailed thermal modeling work. In particular, the transient heat generation rates during moderate and extremely high discharge rate tests of Li–$SOCl_2$ cells were predicted and compared with those from the electrochemical heating. The difference between the two may be attributed to lithium corrosion and other chemical reactions. The present program was also evaluated in charging tests of Li–SO_2 cells. In addition, the present methodology should be applicable, with minor modifications, to analyses of other primary cylindrical cells as well as rechargeable batteries.

Introduction

The present investigation is an extension of our earlier work on a simple transient model that used the lumped heat-capacity method to predict the time-dependent cell temperatures of primary lithium–thionyl chloride (Li–$SOCl_2$) cells [1]. The thermal impact of internal thermal resistances on the overall heat dissipation, however, was not included in the previous analysis. In addition, the heat transfer coefficient, h, which is a function of temperature and position, was assumed to be constant in the previous study to demonstrate the validity of methodology.

The purpose of the present thermal modeling work was to develop a computer program to take into account the effects of internal thermal resistances, non-linear heat transfer coefficients, and radiation in order to identify the mechanism of heat dissipation in typical cylindrical lithium cells. In addition, we calculated the net amount of heat generated from the cell during the discharging or charging procedure, in order better to understand the safety problems of Li–$SOCl_2$ and Li–SO_2 (lithium–sulfur dioxide) battery systems.

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Frank *et al.* pointed out in their study of safety hazards associated with the charging of Li–SO_2 cells [2] that the cell safety depended on a number of variables such as cell type, charging current, temperature, and cell condition prior to charging (discharge history), etc. Results of the charging tests were reduced to the form of a curve called a "safety envelope" that related time-to-explosion with charging current. The time required to reach a dangerous condition increased as the charging current was reduced. Hence, one of the objectives of the present investigation was to calculate the threshold time, which will allow the reliable prediction of the dangerous region for a system without first conducting extensive experimental measurements.

The available experimental data for Li–SO_2 cells were in the form of instantaneous cell wall temperatures and operating cell voltages at a given charge current. All charging tests were carried out with power supplies adjusted to provide a constant current, thus allowing voltages to float. During the charging tests the cells were placed in controlled-temperature chambers so that the ambient temperature remained constant during the tests.

Description of the program

Two computer programs were developed for the present thermal modeling work. Program A calculates instantaneous heat generation rates using the cell wall temperatures as experimental input during discharging or charging tests, while program B calculates instantaneous cell wall temperatures from heat generation rates available from calorimetric measurements. In both cases the internal temperature distribution within the cell is automatically produced. Also, electrolyte consumption schedules were given as input such that a dry or flooded cell could be simulated. The correct estimation of electrolyte during discharging or charging is important in the calculation of the thermal mass of a cell, since electrolyte usually accounts for more than fifty percent of the total thermal mass in the fully discharged condition.

The programs were written in "Basic" and can be run on IBM PC computers. Both programs are fully self-contained and the only input data required are either the transient cell wall temperature for program A or heat generation rate obtained from the calorimetric measurement for program B.

These computer programs were developed as tools with which one can carry out a computer experiment to identify several important safety problems such as the effects of the ambient temperature, the time required to reach a dangerous condition, the discharge or charge current, the amount of electrolyte, etc. To do this, one needs a set of data of both instantaneous cell wall temperatures and heat generation rates obtained from the calorimetric measurement during discharging or charging tests for each particular type of cell. Once the base line test conditions are established for the computer simulation by cross-checking the predicted temperature with experimental data, one can conduct a series of parametric studies by changing one parameter at a time, such as ambient temperature, charging current, amount of electrolyte, etc.

In the following section, the thermal modeling work will be described in detail to indicate the full capabilities and limitations of the computer simulation based on the present thermal model.

Description of the thermal modeling

From the heat transfer point of view, the total amount of heat generated from the cell can be expressed by the sum of the sensible heat stored within the cell and the heat dissipated via convection and radiation. Although the heat transfer coefficient by a forced convection can be larger than that by natural convection by an order of magnitude, the former was not considered here because forced convection cooling requires power from the primary battery system, thus diluting the available power density. Hence, the convection in the present thermal modeling work is natural.

When the cell wall temperature is near the ambient temperature, the heat dissipation by radiation is considered to be relatively small. However, with increasing cell temperature, the amount of heat to be dissipated by radiation is significant. This is true even when the cell temperature is only in the 80 - 120 °C range, as illustrated in Fig. 1 which shows the temperature *versus* time for a D-size Li–$SOCl_2$ cell with a heat generation rate of 10 W. The solid points in Fig. 1 represent the heat dissipation by convection only, while the open points include heat dissipation by radiation. As demonstrated, if radiation is not included in the heat dissipation analysis, the predicted temperature is well above the actual level by almost a factor of two even in the 80 - 120 °C range. Thus, the radiation mode of heat dissipation is kept in the present thermal modeling.

The total amount of heat generated from the cell during a discharging or charging test can be written as

$$Q_{TOTAL} = Q_{CV} + Q_{R} + Q_{S1} + Q_{S2} \quad (1)$$

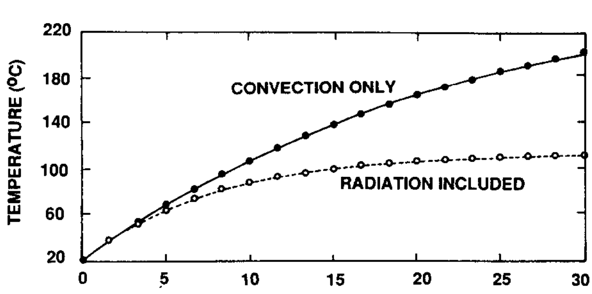


Fig. 1. Predicted temperatures for a D-size Li–$SOCl_2$ cell with a heat generation rate of 10 W. ●, Convection only; ○, radiation included.

where Q_{CV} represents the heat dissipation to the surroundings by convection, Q_R the heat dissipation to the surroundings by radiation, Q_{S1} the sensible heat (energy stored within the cell), and Q_{S2} the sensible heat correction due to the internal temperature variation by heat conduction.

The heat balance equation can be rewritten in terms of the actual parameters:

$$Q_{TOTAL} = hA(T_w - T_a) + F_{1-2}\epsilon\sigma A[T_w^4 - T_a^4] + C_pM\frac{dT}{dt} + Q_{S2} \quad (2)$$

where T_w and T_a are the cell wall temperature and the ambient temperature, respectively. Since Q_{S2} includes the thermal resistance network introduced by Cho (*i.e.*, Fig. 8 [3]) and associated heat conduction analysis, the last term could not be expressed explicitly here. The other terms are described below.

Heat convection

The first term in eqn. (2) represents the amount of heat removed from the cell surface to the environment via natural convection. In the cylindrical cell shape, there are three different areas; the side, top and bottom surfaces. The heat transfer coefficient from each surface is quite different and is a non-linear function of the wall temperature, which again varies with time. Note that the natural convection phenomena from the side, top and bottom walls of the cylindrical cell shape are well established. Hence, using the available experimental data, the dimensionless heat transfer on each wall surface was calculated as a function of the Prandtl and Rayleigh numbers, leading to the calculation of the Nusselt number. The mathematical expressions of the Nusselt numbers in the side, bottom and top surfaces were given by Cho [3]. In addition, the Prandtl number, the thermal conductivity of air and the values of $g\beta/\nu^2$ necessary for the calculation of the Rayleigh number were given as a function of temperature by Cho [3]. This was converted into the corresponding heat transfer coefficient using a characteristic length such as the cell height or diameter. Using the local heat transfer coefficient, the amount of heat convected out from each wall surface was calculated and summed together to produce the total heat convected to the surroundings.

The bottom wall surface posed some uncertainty because the cell could be placed on top of a plastic, wood, or metal shelf during the discharge or charge tests, thus preventing natural convection from occurring from the bottom wall. Depending on the shelf material and the contact resistance between the cell bottom surface and the shelf, the conduction heat transfer from bottom surface to shelf could vary significantly. However, the effect of the shelf was not considered in the present thermal modeling, and heat was assumed to be removed from the bottom wall by the natural convection mode alone. Of note is that from the calculation of the present thermal modeling, the heat dissipation from the bottom wall by convection was found to be relatively small compared with those from the side.

When one has a fairly large size heat sink under the bottom wall, the effect of the heat sink can be significant and should be carefully examined. However, in many aerospace applications, the addition of a heat sink is considered not to be beneficial due to the associated weight gain, which is directly related to the launch cost. Also, note that for a multi-cell arrangement as found in most practical applications of these lithium cells, the active surface area available for heat convection (and radiation) is less per cell than a single cell condition. Thus, the heat convection calculation based on the actual cell arrangement should be carried out to estimate the correct amount of heat dissipated by convection. The multi-cell analysis should constitute future work.

Heat radiation

The second term, radiation heat, represents the energy dissipated by the radiation mode. The amount of radiated energy is proportional to the fourth power of the surface temperature (in the absolute temperature scale) in eqn. (2). Hence, with increasing cell temperature, the role of radiated energy becomes quite important. In general, the amount of heat transferred by radiation depends on the following parameters:

F_{1-2} = configuration factor from wall to the surroundings (geometric constant)
ϵ = emissivity (surface property)
A = active area for radiation
T_w, T_a = cell surface temperature and ambient temperature, respectively.

The values of the configuration factor and the emissivity of the lithium cells used in the present analysis were unity and 0.8, respectively, simulating a single cell test condition. The total surface area of the cell was used as the active radiation area in the present analysis. However, the radiation from the bottom wall should not be included in the analysis when the cell is placed on a shelf. Note that for a multi-cell test one has to calculate the configuration factor using the actual multi-cell arrangement, which could be substantially smaller than unity.

Sensible heat

The sensible energy means the energy stored within the cell due to the temperature rise of a cell during a discharge or charge process. The third term in eqn. (2) represents the product of the total thermal mass and the wall temperature rise during time dt, assuming that the cell internal temperature is the same as the wall temperature.

Cell internal temperatures, however, vary from the cell wall temperature at any given time, t, during the discharging or charging process, caused by the outward heat conduction. Hence, the sensible heat must be corrected to take into account the effects of internal temperature variation within the cell. To determine the local temperature in each cell component at time t, the thermal resistance of each cell component (such as the cathode, anode, separator, electrolyte, and can) was calculated similar to the method introduced by Cho [3]. Accordingly, the sensible heat correction was obtained using the local temperature rise of each cell component. Note that the present program employs the geometry and component materials specifications applying to cylindrical D-size $Li-SOCl_2$ and $Li-SO_2$ cells (*i.e.*, Navy's sonobuoy cell).

In addition, the amount of liquid electrolyte varies with the depth of discharge. Since the thermal mass, defined as the product of mass and specific heat, of the electrolyte is about one third to one half of the total thermal mass of these primary lithium cells, it is very important to provide correct values as a function of time. For example, the electrolyte-limited cell will have almost no liquid electrolyte near the end of discharge, therefore substantially less thermal energy can be stored within the cell near the end of discharge. Hence, the thermal modeling presented here was developed to take into account the effect of actual electrolyte consumption as a function of discharge.

The flooded cell should provide more thermal mass during the discharge process and thus be safer from the heat management point of view than the electrolyte-limited cell. The present thermal model can be used to determine how much better the flooded cell would be compared with the electrolyte-limited cell or how much excess electrolyte is needed to avoid or delay the unsafe condition for a given type of cell. Thus, the initial amount of electrolyte and the consumption rate could be included in the input data.

Results and discussion

Considering the discharge mechanism of the lithium primary cells, the total amount of heat generated from the cell during discharge is the sum of that from the electrochemical reaction and the chemical reactions. In general, the amount of heat from the electrochemical reaction is given by the product of the polarization voltage and the discharge current, while that from the chemical reaction is not well defined.

During the charging procedure, the amount of the total input energy can be expressed as the product of the charging current and the operating cell voltage. Similarly, the excess input energy applied during the charging test may be given by the product of the charging current and the voltage difference between the open circuit voltage (OCV) and the operating voltage. However, it is not known what percentage of the excess input energy is converted into heat. The present thermal modeling work was partly initiated in an attempt to answer this question.

Li–$SOCl_2$ cells

(a) Moderate discharge rate test

A D-size cell was discharged under a constant load of 0.5 ohms. The cell wall temperatures and operating cell voltages were recorded as functions of time and are shown in Fig. 2. The cell wall temperature gradually increased from the ambient of 22 °C to an asymptotic value of 85 °C, while the cell voltage dropped from the maximum value of 3 V at $t = 60$ min to 1.19 V near the end of test (*i.e.*, at $t = 282$ min). The transient cell wall temperature was used as the input for the present program and the corresponding heat generation rate was calculated accordingly.

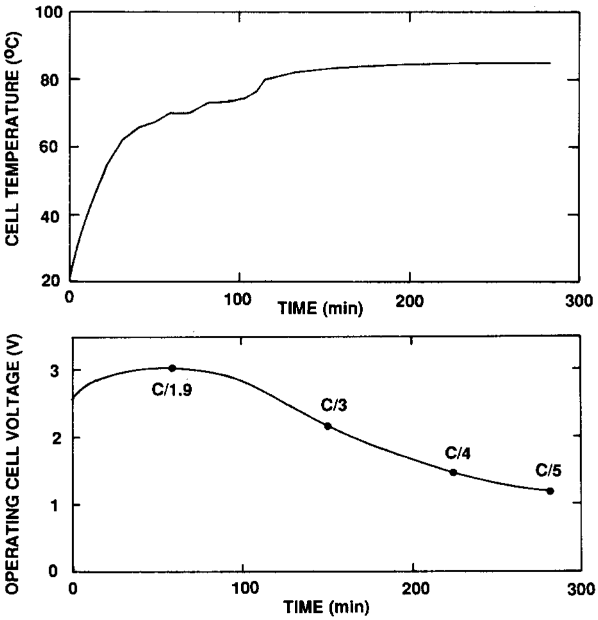


Fig. 2. Experimentally measured cell-wall temperature and operating cell voltage *vs.* time during the discharge test under constant load.

Figure 3 shows the predicted heat generation rate from the present model together with the electrochemical heating based on the thermoneutral potential (E_H) of 3.72 V (see the dashed line in Fig. 3). The predicted heat rate is in good agreement with those calculated with the thermoneutral potential in the range $t = 0$ - 120 min. After $t = 120$ min when the cell operating voltage began to show a substantial drop, the actual predicted heat rate was consistently lower than that of the electrochemical heating, indicating that the electrochemical heating based on the polarization during this period (*i.e.*, approaching the end of discharge) is not a good measure of the total heat produced in the cell.

Figure 4 shows the contributions of the energy used in the form of convection, radiation, sensible energy, and the sensible energy correction due to heat conduction. As shown in the Figure, the sensible energy was dominant

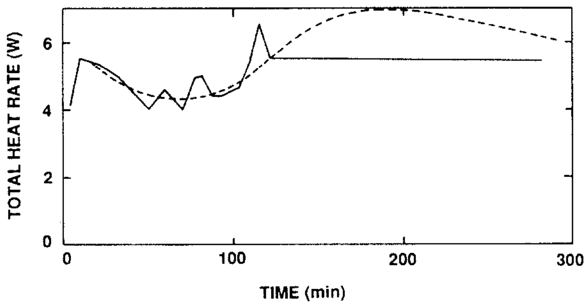


Fig. 3. Prediction of total heat rates from the present model (solid line) and the calculated results based on the thermoneutral potential of 3.72 V (dashed line) for the discharge test under constant load.

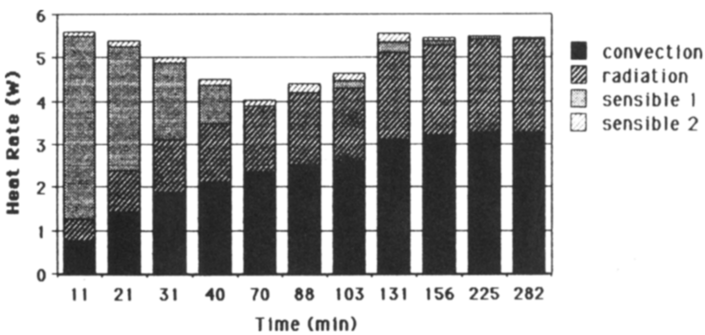


Fig. 4. Contributions of convection, radiation, sensible energy (1), and sensible energy correction due to conduction (2), for the discharge test under constant load.

at the beginning of discharge, while near the end of test convection and radiation accounted for almost all the heat produced within the cell. In addition, the sensible heat correction due to heat conduction was negligible throughout the entire discharge period.

(b) Extremely high discharge rate test

To test the present program, an extremely high discharge rate test was chosen. The mechanism of heat dissipation from the cell was examined for this extreme case. Experimental data were taken from Dey [4] and are shown in Fig. 5, which were obtained by external short circuit using a typical jellyroll type D-size Li–$SOCl_2$ cell. The cell exploded at t = 9.6 min.

The predicted core temperature, together with the experimental wall temperature, is presented in Fig. 6. Prior to the explosion, the temperature difference between wall and core was found to be 28 °C. The core temperature almost reached the melting point of lithium (*i.e.*, 179 °C) while the wall temperature was well below that.

Figure 7 shows the predicted heat generation rate (solid line) and the electrochemical heating based on E_H (dashed line). Note that the electrochemical heating curve was shifted to the right by 0.5 min to match the initial

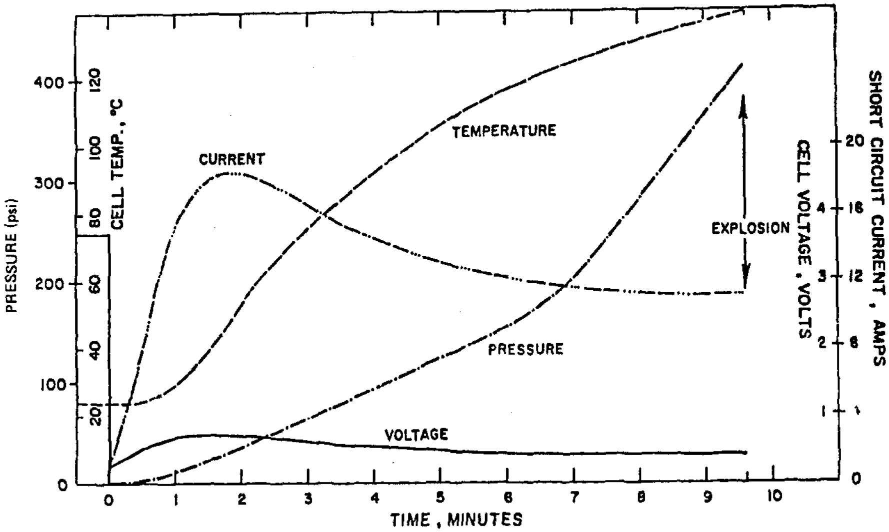
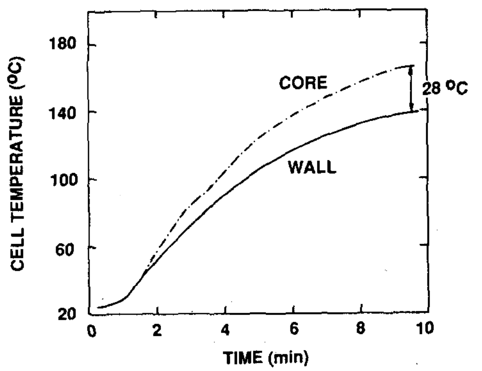


Fig. 5. Experimental data during external short circuit according to Dey [4].



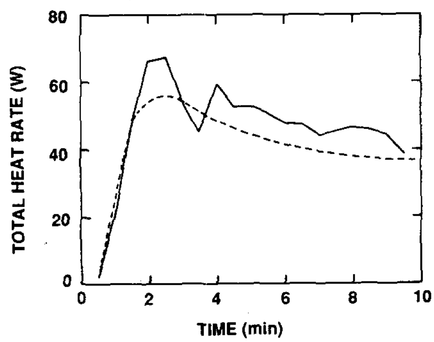


Fig. 6. (Left) Prediction of core and wall temperatures from the present model for the short circuit test.

Fig. 7. (Right) Prediction of total heat rates from the present model (solid line) and the calculated results based on the thermoneutral potential of 3.72 V (dashed line) for the short circuit test.

and predicted slopes. The predicted heat rate was in good agreement with that calculated using E_H, confirming the validity of the present program.

To understand the mechanism of heat dissipation during the extremely high discharge rate test, the contributions of convection, radiation, sensible heat, and sensible heat correction due to heat conduction are shown in Fig. 8. At the start of discharge, the sensible heat accounted for almost all of the heat produced within the cell. However, approaching explosion, the contribution of the sensible heat, Q_{S1}, decreased gradually, while the amount of heat rate due to convection, radiation, and conduction increased. It is interesting to note that the sum of convection and radiation accounted for about

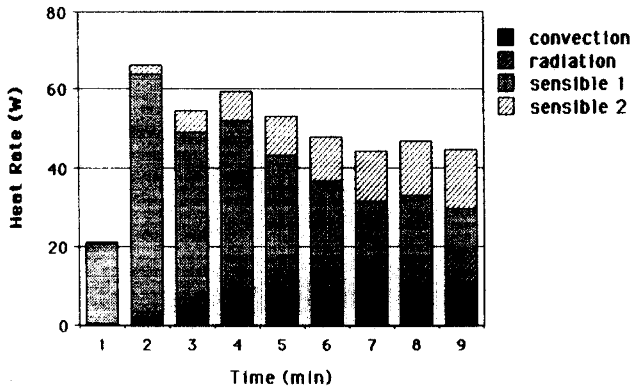


Fig. 8. Contributions of convection, radiation, sensible energy (1), and sensible energy correction due to conduction (2), for the short circuit test.

40%, while conduction accounted for the largest portion of the total heat, approximately 35%. This clearly indicates that one must include the sensible heat correction due to heat conduction in the thermal modeling of high-discharge-rate tests of lithium cells.

Li–SO_2 cells

The present program was considered for charging tests of Li–SO_2 cells. Some of the results will be briefly described. The predicted instantaneous heat generation rate obtained from the Navy's Li–SO_2 cells was found to be smaller than the excess input energy calculated using OCV. The excess input energy is defined as the product of the current and the difference between the cell operating voltage and OCV, $I(E_0 - \text{OCV})$. However, approaching the explosion point, the present model predicted a significant increase in the heat generation rate, suggesting that a vigorous chemical reaction might have started during this period.

Considering the fact that during discharge tests the predicted heat rate was almost equal to, or larger than, the electrochemical heating, the results obtained from the simulation of charging tests showed the opposite trend. The excess input energy was substantially larger than the predicted heat rate, indicating that, during charging tests, a good part of the input energy was consumed in some unknown chemical reactions.

The breakdown of the heat generation rate into convection, radiation, sensible heat, and sensible heat correction due to conduction was also examined. At the beginning and end of the charging test, the sensible heat was large, absorbing a significant percentage of the total heat generated by the cell. During the remainder of the test, however, the sensible heat was found to be very small due to the fact that the cell temperature remained almost unchanged during this period. By contrast, the heat dissipated by convection and radiation was found to increase uniformly with time.

Conclusions

Two programs were developed as tools to investigate the thermal performance of primary lithium cells. Program A predicts the instantaneous heat generation rate while Program B calculates the instantaneous wall temperature. In both cases, internal temperature distributions were automatically produced and the contributions of heat convection, radiation, internal energy stored within the cell (*i.e.*, sensible heat) and its correction due to heat conduction were also identified. These results were used to understand the mechanism of heat dissipation from the lithium cells during discharge or charge tests.

The internal thermal resistance of each cell component was calculated based on the actual design parameters built into the present program. In addition, electrolyte consumption schedules could be given as input such that a dry or flooded cell could be simulated. The major findings are briefly given below:

(i) During discharge tests, the predicted heat rate was in good agreement with the results obtained with electrochemical heating based on the thermoneutral potential, $I(E_H - E_0)$.

(ii) Under normal discharge rate conditions, convection and radiation were dominant heat dissipation modes.

(iii) Approaching an explosion, or for extremely high discharge rate cases such as external short circuits, convection and radiation accounted for only 40% of the total heat produced.

(iv) During most of the charging test, the predicted heat generation rate was found to be consistently less than the excess input energy given by $I(E_0 - \mathrm{OCV})$. However, approaching the explosion point, the predicted heating rate showed a significant increase, suggesting a vigorous chemical reaction occurring within the cell.

(v) Time-histories of convection, radiation, sensible heat, and conduction were calculated from the thermal modeling analysis of both $Li-SOCl_2$ and $Li-SO_2$ cells, helping better to understand the overall thermal behavior of the cell during discharge/charge tests.

A series of parametric investigations using the present thermal modeling program might help to identify the unsafe operating conditions of primary lithium cells. The present program is applicable to other cylindrical primary cells with minor modifications. In addition, the present methodology should be valid for prismatic or button type lithium cells as well as for rechargeable battery analyses in general.

Acknowledgement

The support of the Jet Propulsion Laboratory, California Institute of Technology, is acknowledged by Y.I.C.

List of symbols

A	Cross sectional area
C_p	Specific heat
E_H	Thermoneutral potential of the lithium cell
E_0	Operating cell voltage
F_{1-2}	Configuration factor used in radiation analysis
h	Convection heat transfer coefficient
I	Current
M	Mass of cell
OCV	Open circuit voltage
Q	Heat generation rate
T	Temperature
t	Time
ϵ	Emissivity
σ	Stefan–Boltzman constant

Subscripts

a	Ambient
w	Cell wall

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