

Electricity–heat power and energy balance for Li/SOCl₂ batteries

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Abstract

The heat management equation based on reaction enthalpy and experimental results has been investigated for Li/SOCl₂ cells. The quantity of thermal resistance by experiment has been compared with the theoretical prediction. We define the critical temperature and pressure using phase equilibrium diagram in liquid and vapour; for sulfur dioxide, these values are 157.8 °C and 7.87 MPa, respectively.

Keywords: Lithium batteries; Thionyl chloride; Heat management

1. Introduction

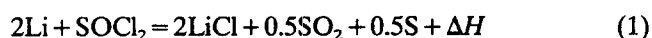
It is of great importance to find optimum methods to realize more efficiently heat management and safety for lithium/SOCl₂ cells. Cho and co-worker [1,2] have obtained values for heat balance, thermal resistance, and the amount of transferred heat. We have studied the performances of chemical thermodynamics for the Li/SOCl₂ cells [3,4]. Evans and White [5] have developed a mathematical model to investigate some factors affecting the performance of the cell and its safety. Kalu and White [6] have presented thermal analyses for spirally-wound Li/SOCl₂ cells. Wang et al. [7] and Qiu et al. [8] have reported the results of discharge of a high power lithium cell using 22 and 400 Ah at a C/2 to 2.2C rate. Kuzminkii [9] has also studied a thermal model for lithium cells.

In this paper, we have presented equations for the thermal management and the paths reducing the temperature and pressure of operating cells [7,8], based on the enthalpy of Li/SOCl₂ cell's reaction, and the law of liquid–vapour phase equilibrium, and compared with experimental results.

2. Assumption for electricity–heat power and energy balance

2.1. Power balance formulae

The reaction of the cell can be written as:



The normal enthalpy for the reaction is $\Delta H^\circ = -174.65$ kcal/mol SOCl₂. In order to solve the heat equation, we need to consider current, I , voltage, V , thermoneutral potential, E_{th} , and heat capacity, etc. The discharged profile of a Li/SOCl₂ cell is given in Fig. 1.

In Fig. 1, the straight line \overline{PM} does not include the corrosion heat, while the other part of the curve \overline{OP} shows the corrosion heat when the temperature rises when discharging the cell. The power balance equation for \overline{PM} can be written as follows:

$$\dot{q}_h = \dot{q}_b + \dot{q}_r \quad (2)$$

In Eq. (2), \dot{q}_h expresses the heat generation rate (W), \dot{q}_b the temperature increasing rate for the battery itself (W), and the \dot{q}_r the heat conduction rate. Eq. (2) shows that the generated heat of cell's reaction involves an increase in temperature and a part of the heat is conducted to the surrounding at the same time. If one takes into account the corrosion reaction in a cell, the

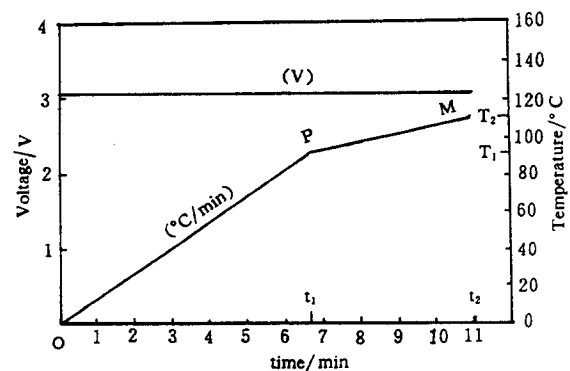


Fig. 1. Ideal performance of the Li/SOCl₂ cell.

heat rate equation must be:

$$\dot{q}_h + \dot{q}_r = \dot{q}_b + \dot{q}_r \tag{3}$$

In Eq. (3), \dot{q}_r is called the corrosion heat rate.

The experiments have indicated that a certain pressure in a high power Li/SOCl₂ cell can be measured when the temperature was higher than 50 °C; the pressure is raised with increasing temperature. Thus, the total heat rate equation can be written as:

$$\dot{q}_h + \dot{q}_r = \dot{q}_b + \dot{q}_r + \dot{q}_{pv} \tag{4}$$

where \dot{q}_{pv} is called the expansion heat rate (W).

2.2. Energy balance functions

The heat generation rate of a practical Li/SOCl₂ cell reaction battery, \dot{q}_h , is:

$$\dot{q}_h = I(E_H - V) \tag{5}$$

where E_H is called the thermoneutral potential (V) for a discharging cell, its temperature can increase continuously, and the thermoneutral potential, $-E_H$ is not a constant $-E_H$ relates to the continuous change in temperature [10]. In Fig. 1, current I and voltage V have a constant value, although E_H is varying and may be presented by an average value. At $-10-80$ °C, $E_H = 3.74 \pm 0.04$ V [10]. When using the value 3.74 V for E_H calculated results is about 2%.

When discharged to time t , the thermal quantity Q_h generated must be equal to:

$$Q_h = I(E_H - V)t \tag{6}$$

where Q_h is the heat generation quantity for the electrochemical reaction in the cell. The profile relating Q to t is given in Fig. 2. The heat quantity Q_h of a electrochemical reaction by enthalpy change has a maximum value. As a matter of fact, the heat Q_b at increasing temperature in an Li/SOCl₂ cell can be higher than Q_h . The range of the increasing temperature heat Q_b for a cell have been given in Fig. 2. From the lines \overline{OP} and \overline{PM} in Fig. 1, Q_b can be calculated as follows:

$$Q_{b1} = \dot{q}_{b1}(t_1 - t_0) = \bar{C}_v W_b (T_1 - T_0) \tag{7}$$

and,

$$Q_{b2} = \dot{q}_{b2}(t - t_1) = \bar{C}_v W_b (T_t - T_1) \tag{8}$$

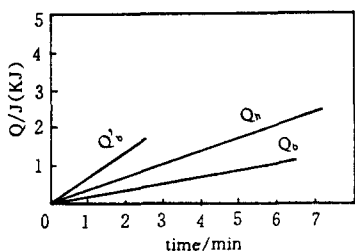


Fig. 2. Ideal generation of heat performance in Li/SOCl₂ cell.

where \bar{C}_v indicates an average specific heat of a battery (J/(g cell)):

$$\bar{C}_v = \frac{\sum_1^n C_i W_i}{W_b} \tag{9}$$

where C_i is the i matter's specific heat, a cell is composed of n kinds of matters, weight W_i ; the temperature T corresponds to the time t . For Fig. 1 the factors t_0 and T_0 equal to zero, thus Eq. (7) will be:

$$\dot{q}_{b1} = \bar{C}_v W_b \frac{T_1}{t_1} \tag{10}$$

where \dot{q}_{b1} equals to a certain constant because temperature versus time is given by the same line. In the same way, the temperature increasing heat rate \dot{q}_{b2} is also equal to a certain constant. We can take back the Eqs. (5) and (10) into Eq. (2) ignoring the corrosion heat:

$$\dot{q}_r = \dot{q}_h - \dot{q}_b = I(E_H - V) - \frac{\bar{C}_v W_b (T - T')}{t - t'} \tag{2b}$$

The terms \dot{q}_h and \dot{q}_b can also be a certain constant so the heat conduction rate \dot{q}_r is also a certain constant.

The cylinder wall heat conduction rate equation can be described as:

$$\dot{q}_r = \frac{T_w - T_0}{R} \tag{11}$$

where the wall temperature, T_w , and the environment temperature, T_0 , represent a stable heat source; R is called the thermal resistance of Li/SOCl₂ cell [1], a quantity that decreases theoretically with increasing temperature. Therefore, the thermal resistance R is not a certain constant. Further, we consider that the heat conduction rate ought to relate to the changing thermal resistance, Eq. (11) can be written as:

$$\dot{q}_r = \frac{dT(t)}{dR(T)} \tag{12}$$

From the curves \overline{OP} and \overline{PM} in Fig. 1 the term \dot{q}_r can be calculated as:

$$\dot{q}_r = \frac{\int_{t_1}^{t_2} dT(t)}{\int_{T_1}^{T_2} dR(T)} = \frac{T_2 - T_1}{R_2 - R_1} \tag{13}$$

Since Eq. (2b) shows that \dot{q}_r is a constant, \dot{q}_r in Eq. (13) must also equal to a certain constant, thus conduction thermal mass Q_r is written as follows:

$$Q_r = \dot{q}_r (t_2 - t_1) = \frac{T_2 - T_1}{R_2 - R_1} (t_2 - t_1) \tag{14}$$

In Eq. (2) the terms \dot{q}_h , \dot{q}_b and \dot{q}_r all equal to a certain constant, we can bring them into Eq. (3), and the corrosion heat rate \dot{q}_r also becomes a certain constant. The corrosion heat mass, Q_r , is written as:

$$Q_r = \dot{q}_r t' \tag{15}$$

In Eq. (15) the sign t' represents the corrosion time.

Bringing Eq. (3) into Eq. (4), then the heat expansion rate \dot{q}_{pv} will equal to a certain constant. The expansion energy, Q_{pv} , is written as:

$$Q_{pv} = \dot{q}_{pv} t'' \tag{16}$$

In Eq. (16), t'' represents the increasing time of total pressure in the Li/SOCl₂ cell.

Based on above-mentioned assumptions we can carry out the total energy balance equation using the results of Eqs. (6), (7), (14)–(16) as:

$$I(E_H - V)t + \dot{q}_r t' = \bar{C}_v W_b (T_i - T_0) + \frac{T_i - T_0}{R_i - R_0} t + \dot{q}_{pv} t'' \tag{17}$$

Eq. (17) can be written as follows:

$$T_i - T_0 = \frac{I(E_H - V)t + \dot{q}_r t' - \dot{q}_{pv} t''}{\bar{C}_v W_b + t/(R_i - R_0)} \tag{17a}$$

In Eq. (17), time t depends on the capacity C_b of a Li/SOCl₂ cell, by the Faraday's law:

$$t \leq C_b / I \tag{18}$$

Eq. (18) is called the heat management equation that can be used to analyse the factors affecting the safety of a Li/SOCl₂ cell.

3. Experimental

The cell's parameters as heat resistance, conduction heat rate, expansion heat, etc., have been calculated using Eq. (17a) according to papers that reported experimental performances [7,8].

4. Results and discussion

4.1. Example 1

The discharged results for ER-22 Ah cell [8] showed that the voltage (V) was more stable at a C/2 rate, the temperature curve can be drawn into two straight lines. The venting pressure was defined in 1.8–2.3 MPa (Fig. 3). The function of heat resistance, R_t , to temperature, T_t , has been drawn in Fig. 4 using $E_H = 3.74$ V, the average specific heat $\bar{C}_v = 0.782$ J/(g °C), weight

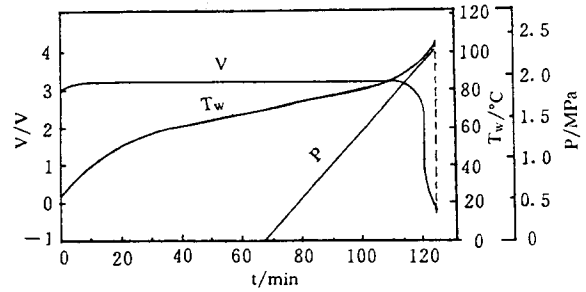


Fig. 3. Discharged results for ER-22 Ah Li/SOCl₂ cell at C/2 rate.

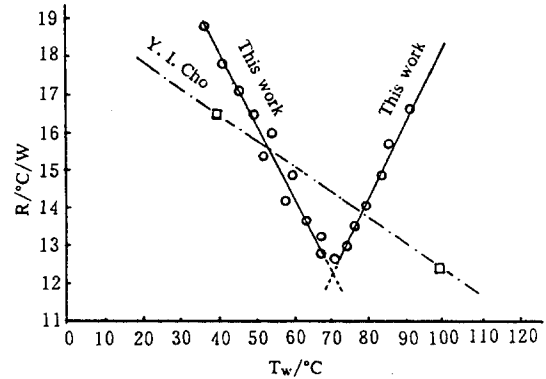


Fig. 4. Thermal resistance (R) vs. temperature T in ER-22 Ah Li/SOCl₂ cell.

$W_b = 230$ g, etc. These heat resistance values decrease with increasing temperature (Y.I. Cho line). However, this value has two aspects: (i) it is decreased with increasing temperature at lower temperatures than 70 °C, in agreement with data reported by Cho [1], and (ii) it is increased with increasing temperatures above 70 °C, that indicated changes of the form of some reactants and products in the battery (liquid SOCl₂ have changed into solid Li-Cl, S and vapour SO₂, etc. The heat resistance of the lithium cell can be calculated from the slope of each straight line:

$$R_t = \frac{1}{\dot{q}_r} T_t + R_0 \tag{19}$$

Eq. (19) is called the thermal resistance equation that gives the relationship of the thermal resistance with the operating temperature; R_0 is the starting thermal resistance.

All parameters of the thermal management Eq. (17a) for ER-22 Ah Li/SOCl₂ cell are given in the Table 1.

The rate of temperature increase results in a quick increase when the corrosion reaction produced extra heat mass. The heat conduction rate is almost constant. The slope of the thermal resistance has a direction presenting a discharging heat character. Although the expansion heat mass was small, it can result in a high pressure of about 1.5 MPa at the wall temperature of 100 °C. Based on physical properties of a phase equi-

Table 1
Thermal management factors for ER-22 Ah Li/SOCl₂ cell

t/min	0–123	0–15	15–123
$T/^\circ\text{C}$	25–90 (wall)	25–70	70–90 (wall)
Heat rate	Ideal	Experiment	
\dot{q}_h (W)	5.93	5.9	5.9
\dot{q}_b (W)	0.90	5.0	0.90
\dot{q}_r (W)	5.03	5.0	5.26
\dot{q}_t (W)	0	4.1	0.23
\dot{q}_{pv} (mW)	0	→0	44
Rate temperature increase ($^\circ\text{C}/\text{min}$)		1.7	0.3
Thermal resistance equation		$R = -0.2T + 26$	$R = 0.19T - 0.80$

Table 2
Thermal management factors for MF-400 Ah Li/SOCl₂ cell

t (min)	0–22	0–14	14–22
T ($^\circ\text{C}$)	15–157 (inner)	15–133	133–157 (inner)
Heat rate	Ideal	Experiment	
\dot{q}_h (kW)	0.414	0.41	0.41
\dot{q}_b (kW)	0.20	0.85	0.19
\dot{q}_r (kW)	2.14	0.20	0.21
\dot{q}_t (kW)	0	0.63	→0
\dot{q}_{pv} (W)	0	0.06	0.06
Rate temperature increase ($^\circ\text{C}/\text{min}$)		(> 50 $^\circ\text{C}$) 8.9	2.0
Thermal resistance equation		$R = 5.17T - 116$	

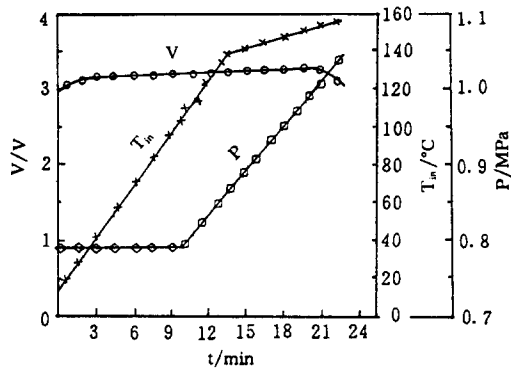


Fig. 5. Operating characters of MF-400 Ah cell at 2.2C rate.

librium for sulfur dioxide, the critical temperature and pressure are 157.8 $^\circ\text{C}$ and 7.87 MPa, respectively.

4.2. Example 2

The discharged results of MF-400 Ah Li/SOCl₂ cell have been drawn in Fig. 5. The weight is 7.11 kg, average specific heat \bar{C}_v is 0.804 J/(g $^\circ\text{C}$) (including liquid vaporation, sulfur phase change, vapour heat capacity, etc.), and the thermoneutral potential E_H is 3.735 V. The parameters of the thermal management

Eq. (17a) for MF-400 Ah Li/SOCl₂ cell at a 2.2C rate are given in Table 2.

The change in heat resistance is different for high power and capacity lithium cells compared with normal small cells. Here, only the thermal resistance increases with increasing temperature. The gas pressure of the cell was much lower compared with that of the ER-22 Ah cell, because the percent power of MF-400 Ah cell versus the expansion energy generating heat have decreased about 100 times. This pressure of vapours depends on form and amount of cell's matters, SO₂ and Cl₂. When these matters are vapoured heavily but the amount was less, the pressure would be small. It should be emphasized that the corrosion heat is in origin resulting in the temperature increase to 130 $^\circ\text{C}$. Raising the temperature heat rate, \dot{q}_b in first part for the lithium cell is about four times than in second part. If the corrosion heat would be decreased greatly or even eliminated, the cell's operating temperature will be not high.

It should be noted that all factors of the thermal management can be used only as a reference when the investigator plans to design a safe lithium cell with a liquid cathode.

5. Conclusions

1. The thermal management equation can help to analyse the factors influencing the safety of a lithium cell.

2. The values of thermal resistance relate to properties of a cell's reaction. They can increase with increasing temperature, and also decrease.

3. The corrosion heat can increase the cell's temperature by 65% higher than normal.

4. The expansible potential heat can provoke a battery explosion. This may be prevented as long as the temperature and pressure do not exceed or are close to the critical value of liquid–vapour phase equilibrium.

References

- [1] Y.I. Cho, *J. Electrochem. Soc.*, 134 (1987) 771–779.
- [2] Y.I. Cho and G. Halpert, *J. Power Sources*, 18 (1986) 109–115.
- [3] Z.-D. Wang, *Ext. Abstr.*, 7th Meet. Electrochemistry, ChangChun, China, 1993, p. 190.
- [4] Z.-D. Wang, *Batteries*, to be published.
- [5] T.I. Evans and R.E. White, *J. Electrochem. Soc.*, 136 (1989) 328–339.
- [6] E.E. Kalu and R.E. White, *J. Electrochem. Soc.*, 140 (1993) 23–31.
- [7] J. Wang et al., *Ext. Abstr.*, 6th Int. Meet. Lithium Batteries, Münster, Germany, 10–15 May 1992, p. 154.
- [8] R. Qiu et al., *Ext. Abstr.*, 5th Int. Meet. Lithium Batteries, Beijing, China, 1990, p. 268–271.
- [9] Ye.V. Kuzminskii, *Ext. Abstr.*, 6th Int. Meet. Lithium Batteries, Münster, Germany, 10–15 May 1992, p. 301–306.
- [10] N.A. Godshall and J.R. Driscoll, *J. Electrochem. Soc.*, 131 (1984) 2221–2224.