

Thermal modelling of a high power Li/SOCl₂ cell with parallel plates

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Abstract

A thermal model has been proposed for a high power Li/SOCl₂ cell with parallel plates. Internal temperature profiles in two types of cells have been obtained by calculations based on the model and the experiment. Results show that model predictions are very consistent with experimental data provided the calculations are carried out under certain conditions.

Background

Li/SOCl₂ cell is an attractive primary energy source because of its high energy density [1, 2]. However, it was shown from previous results that high discharge rates and high temperature promoted thermal runaway in these cells [1-5]. Therefore, many researchers have dealt with the thermal behavior of the cells.

Evans and Nguyen [6] developed a one-dimensional mathematical model for the Li/SOCl₂ primary cell to investigate methods of improving its performance and safety. Later Evans and White [7] proposed a two-dimensional thermal model for spirally-wound 'D-size' Li/SiOCl₂ cells and presented an internal temperature profile calculated by computer package called TOPA2D under a certain discharge condition. Parnell and Szpak [8] developed a thermal model for batteries of a thin-cell design. Young I Cho carried out a thermal resistance network analysis by assuming all the components of JPL 'D-size' Li/SOCl₂ cell as thermal resistance components and described the thermal behavior of the cell by calculating thermal resistance value of each component. Computer-aided design programs were developed by SAFT to support the design of Li/SOCl₂ reserve type of torpedo batteries [9].

The purpose of this paper is to present a thermal model for a high power Li/SOCl₂ cell with parallel plates designed and tested in our laboratory and to carry out thermal analysis to predict a temperature profile within the cell under a certain condition as well as to make a preliminary comparison of experimental data with predictions.

Mathematical basis on the cell temperature field

The basic differential equation of heat transfer according to energy balance can be written as:

$$\text{div}(k_{\nabla}T) + q = \rho C_p \frac{\partial T}{\partial t} \quad (1)$$

where C_p , ρ , and k are the specific heat, density and thermal conductivity, respectively; q is the heat generation.

The convection boundary condition is specified as follows:

$$-k \frac{\partial T}{\partial n} = h(T_w - T_{\infty}) \quad (2)$$

where T_w is the temperature of the cell as its outer wall, T_{∞} the surrounding temperature, h the heat transfer coefficient, and n the normal vector.

The classic method being used to solve instantaneous heat conduction is a nodal point network method.

Based on the differential eqn. (1), using finite difference to replace the differential eqn. then difference eqn. is made. In this case, the computer package called TAP6 can be directly used to solve difference eqn. and the thermal behavior of the cell can be investigated.

A thermal model of the cell

The structure and geometric parameter of the cell are shown in Fig. 1 and Table 1. It is seen that the plates are parallel arranged inside the cell and the plane dimension of a plate is much larger than that of its thickness. Hence, the heat transfer is mainly carried out between plates. Results calculated based on a three-dimensional network indicate that the temperature within a plate is almost uniformly distributed (maximum temperature difference is about 4 °C between any two nodal points), except the nodal point connected to the tab. In consequence, each plate can be considered as a nodal point and the heat transfer behavior of the cell can be simply described by one-dimensional network model presented in Fig. 2. Due to the symmetry, only a half of the nodal points are expressed.

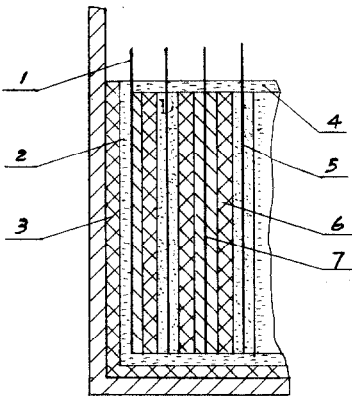
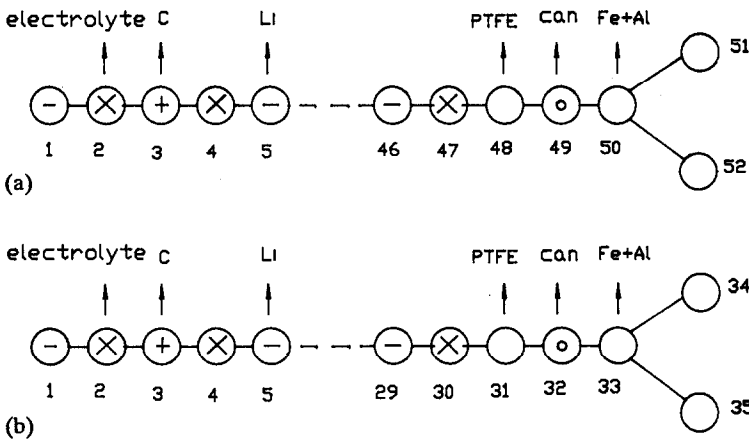


Fig. 1. Cutaway view of a high power Li/SOCl₂ cell with parallel plates: (1) nickel current collector; (2) polytetrafluoroethylene (PTFE); (3) case; (4) electrolyte; (5) carbon electrode; (6) separator, and (7) lithium electrode.

TABLE 1

Geometric parameters of basic components in a high rate Li/SOCl₂ cell with parallel plates

Basic component	Surface area (m ²)		Thickness (mm)
	Case 1	Case 2	
Nickel current collector	0.113	0.12	0.15
Lithium anode	0.113	0.12	^a
Carbon cathode	0.113	0.12	0.7668 (case 1) ^b 0.3762 (case 2)
Separator (two)	0.113	0.12	^c

^aCase 1: 0.12–0.0046 mm/min; case 2: 0.07–0.003 mm/min.^bPorosity of the carbon electrode is changed by 11.7%/min.^cCase 1: 0.08+0.0046 mm/min; case 2: 0.08+0.003 mm/min.Fig. 2. The node network model of a high power Li/SOCl₂ cells: (a) with metal can, and (b) with plastic can.

Basic data required for computerizing

The thermophysical parameters of the cell components are listed in Table 2. The heat generation in the cell can be expressed as follows:

$$Q = Q_p + Q_s + Q_f \quad (3)$$

where Q_p is the heat generated by polarization, Q_s the heat generated due to entropy change of the current producing reactions, and Q_f the heat generated by corrosion.

The heat generation terms Q_p and Q_s are calculated by using the following formula:

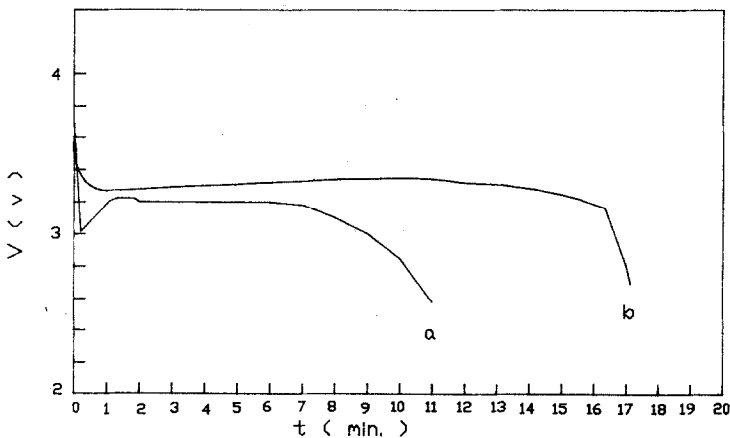
$$Q_p + Q_s = I(E_{th} - V) \quad (4)$$

E_{th} in eqn. (4), termed the thermoneutral potential, is the theoretical open-circuit potential of the cell at absolute zero. The cell voltage, V in eqn. (4) can be obtained from experiment, as typically shown in Fig. 3.

TABLE 2

Thermophysical parameters of components in a Li/SOCl₂ cell with parallel plates

Material	Density (g/cm ³)	Thermal conductivity W/(m K)	Specific heat J/(kg K)
Lithium	0.534	71.2	3490
Carbon	1.95	23.8	712
Nickel	8.91	90.5	444-460
Electrolyte	1.70	0.15	921 (20 °C) 1590 (100 °C)
PTFE	2.24	0.186	1046
LiCl	2.07	23.6	1133
Stainless steel	7.85	16.3	460
Iron	7.75	36.7	470
Aluminum	2.7	236 (0 °C) 240 (100 °C)	902
Glass-fiber reinforced plastic	1.8	0.27	1050
Separator ^a	2.2	0.24	263

^aPorosity of the separator is 80%.Fig. 3. Typical discharge curves of high power Li/SOCl₂ cells with parallel plates: (a) in AlCl₃/SOCl₂ electrolyte ($i=60$ mA/cm²), and (b) in LiAlCl₄/SOCl₂ electrolyte ($i=35$ mA/cm²).

Results and discussion

Computerizing results and analysis of the experimental cell with plastic can

In order to carry on analysis and computerization based on the thermal model, it is very important to obtain the heat generation rate by corrosion varied with discharge time.

In an acid electrolyte system, the corrosion heat reported in literature is 5 cal/cm² [10], but it can not be used directly. Considering q_t is varied with discharge time, an equation is assumed as follows:

$$q_t = A \exp(-\beta t) \quad (5)$$

where A , β are constants, and q_t is the heat generation rate by corrosion.

Figure 4 shows the relation curves of q_t as a function of discharge time. The curves (c) and (b) are corresponding to the total heat, 5 cal/cm^2 distributed among 20 min and among 11 min, respectively. The computerizing temperature profiles calculated by using q_t-t relations of curve (b) and (c) in Fig. 4 are shown as curve (b) and (c) in Fig. 5, respectively.

The computerizing results indicate that the latter temperature profile (curve (c) in Fig. 5) calculated based on the model is rather close to the experimental temperature curve. But, both curve (b) and curve (c) are still far away from the experimental value. It is thought that the heat generation by corrosion needs a transient course and the delay phenomenon may exist in the system of the temperature measurement

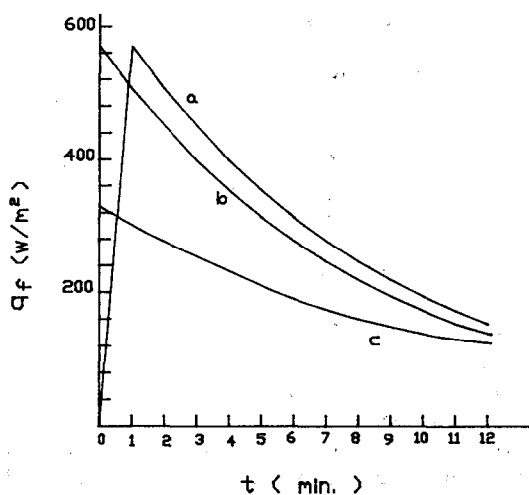


Fig. 4. Relation of the heat generation by corrosion q_t and discharge time t .

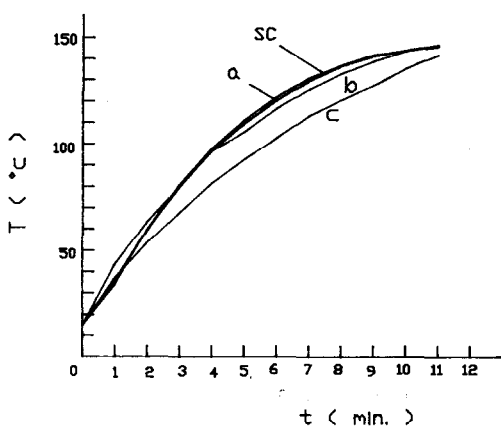


Fig. 5. Temperature profiles of the high power experimental Li/SOCl_2 cell with plastic can; (a), (b) and (c): computerized curves, and (SC): experimental curve.

for the cell. Therefore, it is assumed that from the beginning of the discharge, the heat generated by corrosion rises as fast as the linear function of the time and reaches the maximum at 1 min, then decreases in accordance with eqn. (5), shown as curve (a) in Fig. 4.

According to the calculation from Table 2, the heat capacity of the electrolyte is nearly half of the cell. Therefore, it is one of the primary factors to affect the thermal performance of the cell. More experimental data showed that the experimental cell had leakage apparently when its internal temperature exceeded 120 °C. From the thermal model point of view, the sudden increase of the electrolyte heat capacity at the end of the discharge can be used to simulate the phenomenon of the electrolyte vaporization. After analysing and treating, the temperature profile calculated, based on the thermal model, is very consistent with that of the experiment, see Fig. 5.

Computerizing results and analysis of the cell with metal can

Comparing the cell with metal can and that of the experimental can, the main difference is that the acid electrolyte is replaced by the neutral electrolyte in the metal can cell.

At first, the corrosion heat is assumed zero under calculation. The result calculated based on the thermal model is shown as curve (b) in Fig. 6. It is far lower than that of experimental data. This indicates that the cell with the neutral electrolyte has other heat sources besides the heat generated by polarization during the discharge. Although it has been reported that the corrosion heat in the neutral electrolyte is less than that in the acid electrolyte [11], some experimental results [12] obtained in our laboratory show that the chemical corrosion of the lithium in $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte becomes more significant with the increase of temperature and the decrease of current density during the discharge. In the calculation, the corrosion heat varied with discharge time is then added, as shown in Fig. 7. The cell with metal can is sealed hermetically, the electrolyte cannot vaporize at the end of discharge. Therefore, vaporization phenomenon of the electrolyte is no longer considered. Finally, the temperature profile calculated on the thermal model is very consistent with experimental data, see Fig. 7.

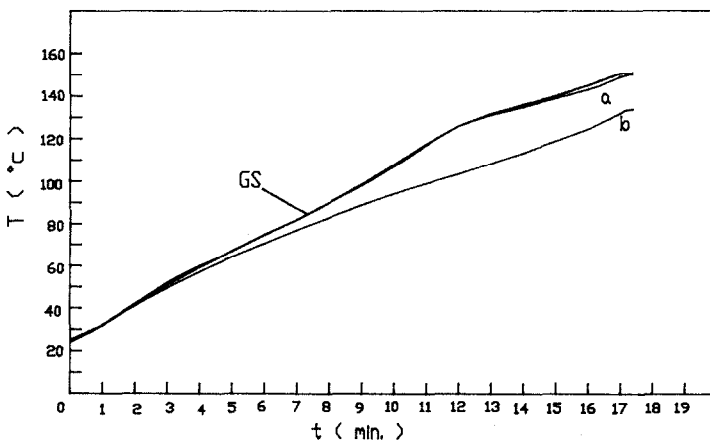


Fig. 6. Temperature profile of the high power Li/SOCl_2 cell with metal can: (a) computerized curve, (GS) experimental curve, and (b) computerized curve, as q_f is assumed to be zero.

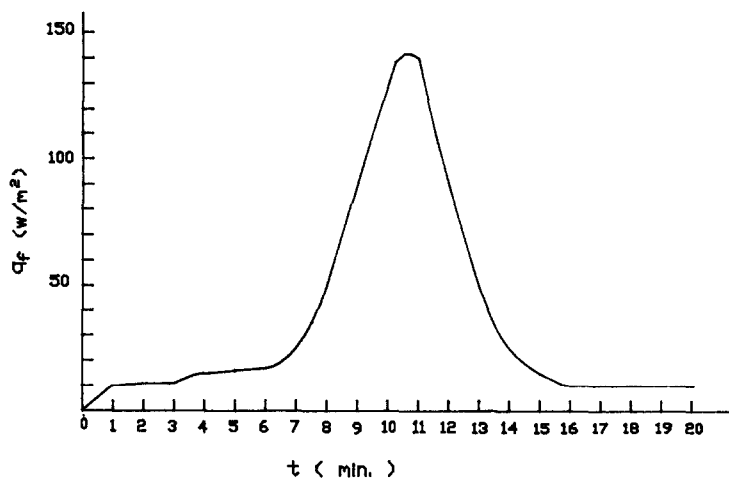


Fig. 7. Dependence of q_f on time in neutral electrolyte.

Conclusions

A three-dimensional and one-dimensional thermal model of a high power Li/SOCl₂ cell with parallel plates have been developed. The computerizing results show that a three-dimensional thermal model can be simplified by one-dimensional thermal model. It is shown from the results that the model predictions are very consistent with experimental data. This model has been used for a better understanding of the thermal behavior of the high power Li/SOCl₂ cell.

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