

# Kinetics of Open Circuit Processes in Undischarged Li/SOCl<sub>2</sub> Cells

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## ABSTRACT

The kinetics of the heat producing processes in undischarged Li/SOCl<sub>2</sub> cells under open circuit conditions have been measured by heat-conduction microcalorimetry. The cells studied, Honeywell type G2666 reserve cells, were activated as needed and the rate of open circuit heat output determined as a function of time since activation and temperature. The results at each temperature can be described by an equation of the form  $q = Bkt^x$  where  $q$  is the rate of heat output,  $B$  is the heat produced per unit of reaction,  $k$  and  $x$  are empirical constants, and  $t$  is the time since activation. Both  $x$  and  $k$  are found to be functions of temperature; therefore, accelerated testing at elevated temperatures is probably not valid for these cells until the processes involved are better understood.

## INTRODUCTION

Shelf life testing of primary batteries is usually done at elevated temperatures in order to shorten the time required for the tests. The results at the elevated temperature are then extrapolated to room temperature. The results of such a procedure are valid provided that no change in the mechanisms of the parasitic processes occurs between room temperature and the temperature at which the tests were done. The work described in this report was designed to determine the kinetic constants necessary for the extrapolation of kinetic data on Li/SOCl<sub>2</sub> cells over the temperature range from 25 to 75°C.

A second objective of the work described in this report was to characterize as far as possible the parasitic processes which occur in Li/SOCl<sub>2</sub> cells since these processes may be important in understanding the potential hazards of these cells.

## MATERIALS

The type G2666 Li/SOCl<sub>2</sub> reserve cells were purchased from Honeywell. These cells are 0.28 amp-hour cylindrical cells approximately 0.5" dia. by 0.8" long. The cell electrolyte, LiAlCl<sub>4</sub> dissolved in SOCl<sub>2</sub>, is contained in a glass ampoule within the cell. The cell is activated when desired by breaking the glass ampoule by denting the stainless steel case in the center of the bottom of the cell.

## EQUIPMENT

The calorimeter used to measure the heat output of the cells was a Tronac Model 351 RA. The constant temperature bath in this

calorimeter has an upper limit of 45°C. Therefore, when measurements were made at temperatures above 45°C the calorimeter insert was moved to a Hart Scientific Model 5024 water bath. The electronics were thermostatted at 25°C in the Tronac air bath during these measurements.

## RESULTS

The results on unactivated cells are given in Table 1. These data show that there was no significant heat production present in the cells prior to activation except at 65°C and above.

The results obtained on cells activated and kept at 25 or 65°C are shown in Figure 1 as a plot of  $\ln q$  against  $\ln t$  where  $q$  is the rate of heat production in microwatts and  $t$  is the time in seconds since activation. These results show that the cells follow a rate law of the form

$$q = Bkt^x \quad (1)$$

where both  $k$  and  $x$  are functions of temperature. The constant  $B$ , the heat produced per unit of reaction, is probably not a function of temperature. The process producing heat under open circuit conditions is probably the direct reaction of Li with  $\text{SOCl}_2$ , the same reaction occurring when the cell is under load. The enthalpy change for the closed circuit cell reaction has been shown to be constant over the temperature range used in this study (1,2).

Figure 2 shows data taken on cells which have been cycled between 25°C and various temperatures up to 75°C. These data indicate that the rate of heat production is a function of the temperature and time since activation, but not of the temperature history of the battery.

## DISCUSSION

At the time this work was begun, it was expected that the kinetics of heat production would follow the kinetics predicted from a parabolic film growth model. Data collected in a previous, but much abbreviated study, had suggested such a possibility (3). Also, much previous work has indicated that the growth of a LiCl passivation layer controls the kinetic properties of Li/SOCl<sub>2</sub> cells (4,5). However, three characteristics of the data in Figure 1 suggest that a parabolic film growth model is either incorrect or at least not sufficient. First, the slope of the  $\ln p$  versus  $\ln t$  curves are not  $-0.5$ ; second, the slope changes with temperature; and third, cells which have been cycled to higher temperatures do not show a decreased heat production rate at lower temperatures when compared to cells which have been held at the lower temperature for the same period of time since activation.

The results of this study clearly show that either the mechanism of the heat producing reaction changes or the relative rates of the heat producing reactions change as a function of temperature. Thus, we are forced to conclude that accelerated testing of Li/SOCl<sub>2</sub> cells must be regarded with suspicion until the parasitic processes are more fully understood so that their kinetics may be modeled as a function of temperature.

## REFERENCES

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Table 1  
Heat Produced by Unactivated Cells

<u>Cell</u>	<u>Temperature, °C</u>	<u>Heat Output, uW</u>
2	25	0.0
3	25	0.0
4	25	0.0
2	55	0.0
3	55	0.0
4	55	0.0
2	65	2.6
3	65	0.9
4	65	1.7

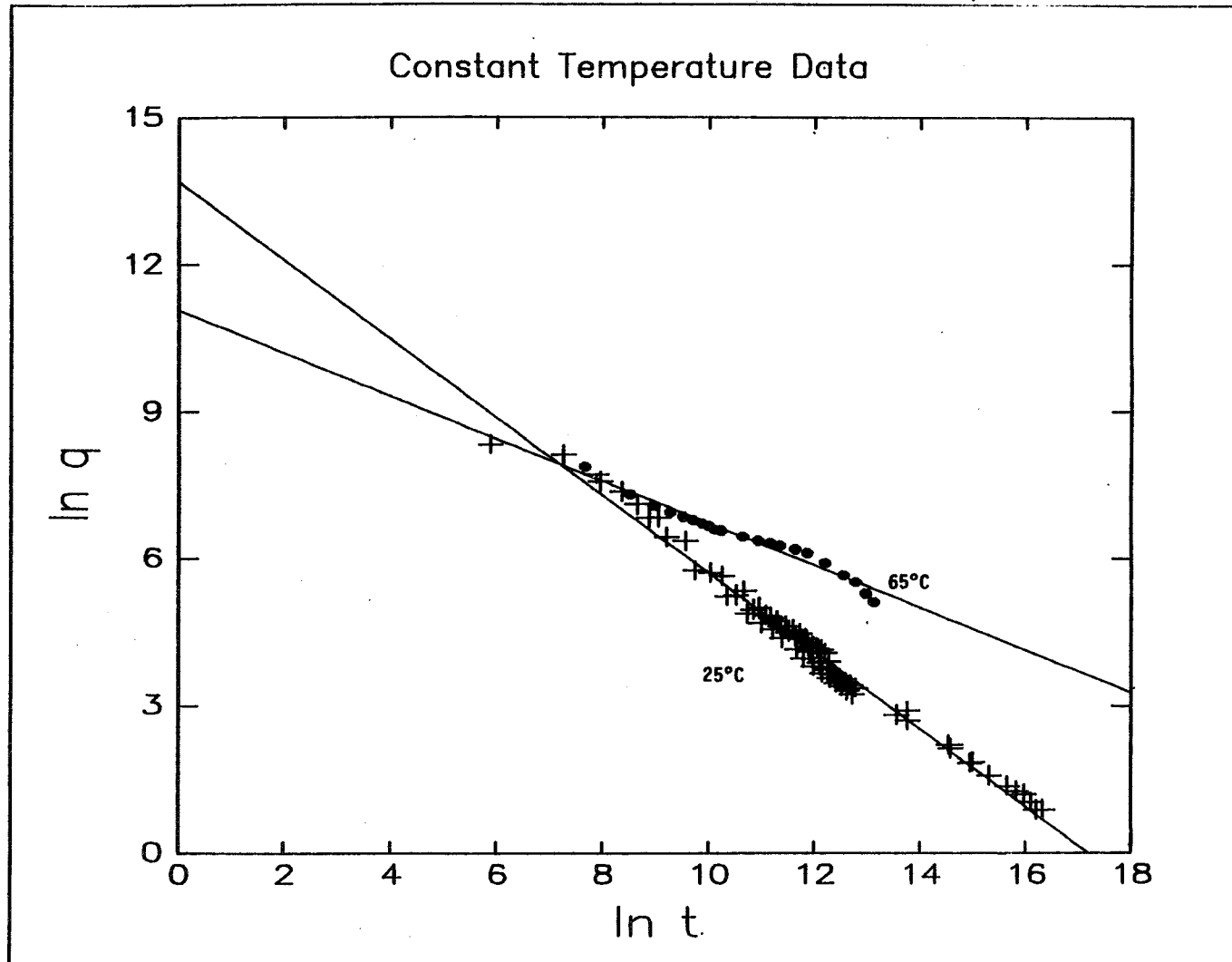


Figure 1. A plot of  $\ln q$ , the rate of heat production in  $\mu\text{W}$ , versus  $\ln t$ , the time since activation in seconds, for cells activated and maintained at constant temperature. The lines are linear least square fits to the data shown.

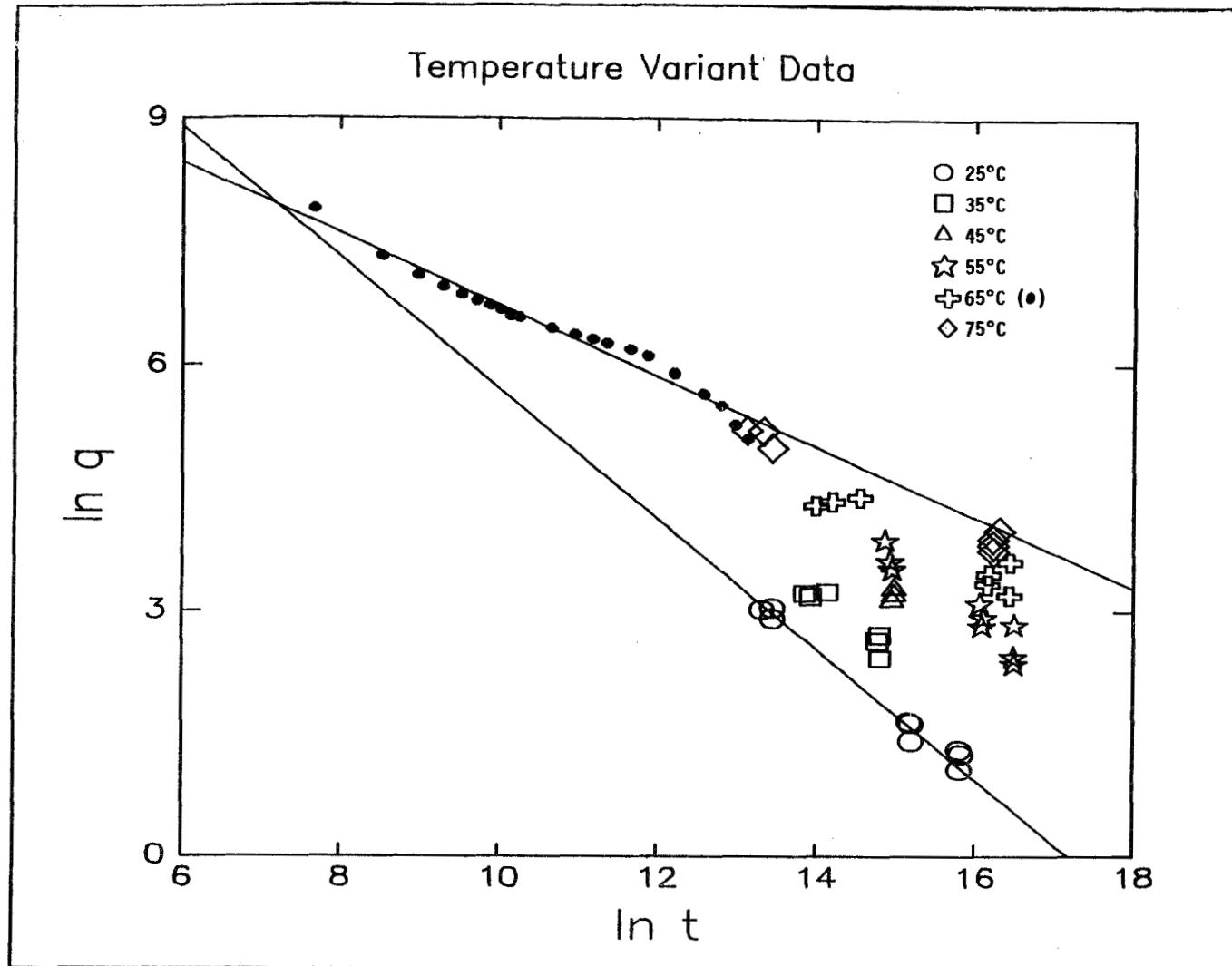


Figure 2. Data taken on cells held at 25°C except during measurement at the indicated temperatures. Measurement at elevated temperature required that the cells be held at the elevated temperature from 1 to 5 days. The lines represent the 25°C and 65°C constant temperature data as shown in figure 1.