THERMAL BEHAVIOR OF ELECTROCHEMICAL CELLS BY LIQUID CRYSTAL DISPLAY

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Summary

A method for the continuous display and monitoring of temperature profiles in electrochemical cells is described. This method employs liquid crystal films formulated for a given temperature resolution.

Introduction

The high energy and power density inherent in the $Li/SOCl_2$ system permit the design of batteries which are significantly more compact than conventional systems. One design which takes full advantage of this high energy density is the bipolar stack, wherein, for example, circular cells are placed one on top of another in a series arrangement. In practice, these cells are relatively thin, with cell thicknesses ranging from 2.9 - 5.1 $\times$ 10^{-4} m

A major consideration in such designs is the management of heat generated during their operation, which arises from cell polarization and lithium corrosion In principle, the magnitude of these sources can be determined with good accuracy. For successful design, however, it is necessary not only to know the magnitude of these sources, but also their spatial and temporal distribution Thermal models of various degrees of sophisticacation have been presented [1, 2], but their predictive capabilities cannot be tested without direct measurement of the evolution of temperature profiles within individual cells.

The purpose of this communication is, first, to describe a cell designed to simulate an operating battery and, second, to present a method for continuous display of temperature profiles evolving during the activation and discharge periods.

B

A

D

ACTIVE
REGION
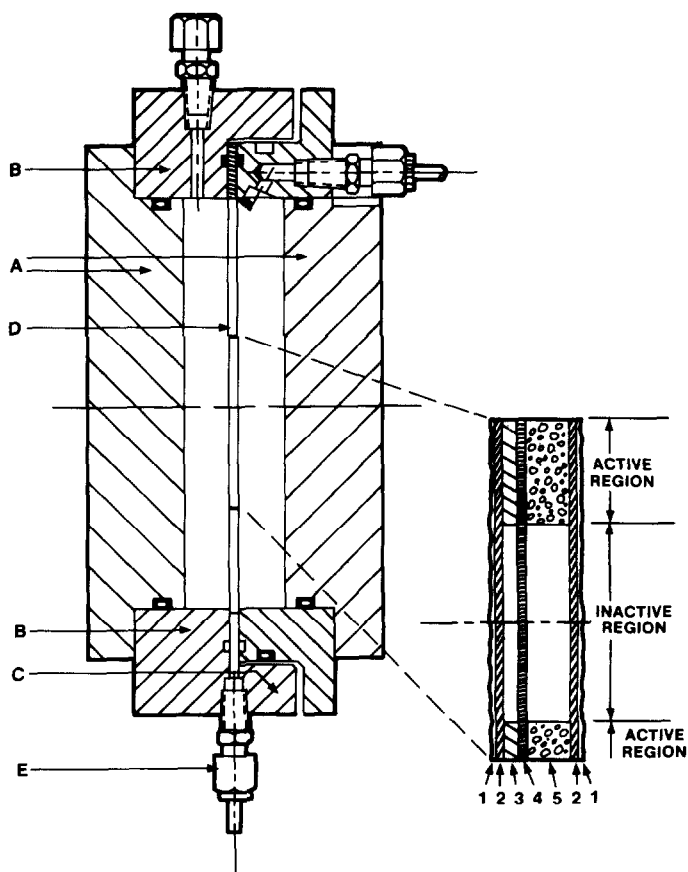
INACTIVE
REGION

B

C

ACTIVE
REGION

E

1 2 3 4 5 2 1

Fig 1 Test cell fixture A, Plexiglass windows, B, inner steel ring, C, outer steel ring, D, cell clamped in position, E, vacuum and electrolyte feed line Insert 1, liquid crystal film, 2, Cu/Ni foil, 3, metallic Li, 4, separator, 5, Shawinigan Black positive electrode Active and inactive regions indicated

Experimental

Li/SOCl₂ cell

An Li/SOCl$_2$ circular cell was constructed and assembled as shown in Fig 1. A single cell, with all pertinent information summarized in Table 1, was placed in a fixture designed to emulate, as closely as possible, conditions existing in a real battery and yet to permit direct monitoring of the time-dependent temperature profiles.

The fixture consisted of two machined, stainless steel rings, one of which slid into the other The lips of each of these rings hold and compress the edges of the metal foil of the cell. Electrical insulation and physical sealing are provided by three O-rings. One O-ring is on the outside — its purpose is to insulate the two electrodes as well as to provide a pressure

TABLE 1

Cell elements

Component	Description	Comments
Li — negative	Thickness 7 6 × 10^{-5} m dia o d 0 102 m i d 0 025 m	
Separator	Inorganic material thickness 2 5 × 10^{-4} m dia 0 108 m	See ref 4
C — positive	Thickness 3 01 × 10^{-4} m dia o d 0 098 m i d 0 032 m Surface density 9 × 10^{-4} kg/m^2 Composition 325 mesh Cu, 20 wt %, Shawinigan black, balance	See ref 5
Ni/Cu foil	Thickness Ni 8 9 × 10^{-6} m Cu 4 3 × 10^{-5} m	
Electrolyte	1 9M (LiAlCl$_4$) 0 3M AlCl$_3$ volume 2 3 ml	

boundary between the internal parts of the cell and its outer diameter. Two other O-rings assure the pressure boundary at the inner diameter of the cell A Plexiglass window is sealed to each of the stainless steel rings, also with O-rings. They create a pressure boundary between the exterior surfaces of the Ni-clad Cu foils of the cell and the external atmosphere, providing a gas-tight chamber on each side of the cell while still permitting viewing of the exterior surfaces of the cell The cell was compressed to its final dimensions of 3 8 × 10^{-4} m by pressurising these two chambers to approximately 1 5 atm with argon gas

Display of temperature profiles

In practice, strategically located thermocouples can be used to follow the time change of temperature profiles. Such an arrangement is satisfactory if (i) changes in temperature are slow, and (ii) the heat source is more or less uniformly distributed throughout the cell. These conditions are met with in well behaved cells — they are not met with in cells with localized defects. A better display of temperature profiles and their changes with time is assured through the use of liquid crystal films

One type of liquid crystal consists of ordered layers of molecules with the spacing between them being a function of temperature. As the spacing changes, destructive and constructive interference occurs at various wavelengths of visible light Under these conditions spatial temperature profiles are displayed by a sequence of colors, from blue (at $t < 30$ °C) through blue–

green (30 - 37 °C), green (37 - 45 °C), yellow–green (45 - 50 °C), red–yellow (55 - 60 °C) to red at temperatures in excess of 60 °C

Two solutions of a proprietary nature (Davis Liquid Crystals, Inc., San Leandro, CA 94577, USA) were formulated to provide for an adequate resolution over the range of anticipated temperatures in a preselected set of experiments Good quality films were obtained by an air brush application of these solutions followed by the evaporation of solvent at 40 °C for *ca* 15 min. To assure high sensitivity, the evaporated films were heat treated at 120 °C for a period of 10 - 20 s The state of high sensitivity of these liquid crystal films is not permanent and, consequently, experiments must be completed within an hour.

Experimental arrangement and procedure

Cell components were assembled into the fixture in a dry room (RH ≤ 1%) The external fixture chambers were pressurized with argon to about 1.5 atm, followed by the evacuation of the test cell to *ca* 10 - 20 mTorr After approximately 5 min, an acidic electrolyte (1 9M $LiAlCl_4$ + 0 3M $AlCl_3$ in $SOCl_2$) was admitted. As a rule, the cell was allowed to stand on open circuit for about 3 min before the cell discharge through a constant resistive load was initiated.

The experimental set-up, in the form of a block diagram, is shown in Fig. 2 The temperature distribution across the cell face was recorded by repetitively photographing the patterns of color in the liquid crystal films It is noted that the lighting arrangement is fairly important for enhancing the recording of the changing color pattern.
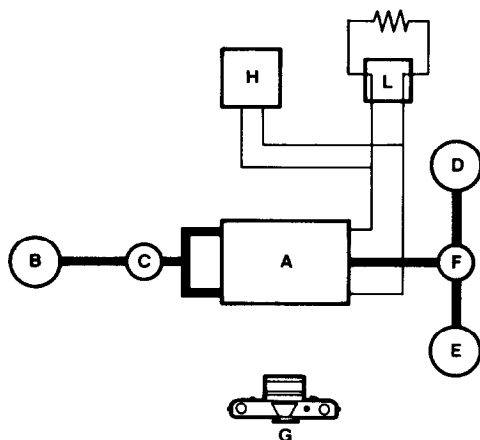

Fig 2 Block diagram of the experimental set-up A, Cell test fixture, B, adjustable argon gas supply, C, valve, D, electrolyte supply, E, vacuum, F, two way valve, G, camera, H, strip chart recorder, I, resistive load

Results and discussion

Two cases are illustrated: radial temperature distribution in well behaved cells and evolution of temperature profiles in cells with intentionally built-in defects

Well behaved cells

Ten cells were discharged under normal conditions, in duplicates, at current densities ranging from 60 to 100 mA cm^{-2} at 10 mA cm^{-2} intervals. The results are given in Table 2. A representative cell voltage–time curve and the temperature profiles are shown in Figs 3 and 4, respectively.

A comparison of the present data with those of standard laboratory cells, as well as production stacks of the same configuration, shows excellent agreement, Fig 5 This agreement indicates that the mounting of a cell in the manner illustrated in Fig 1, reliably reproduces conditions existing in practical bipolar stacks. The usual assumption of no temperature difference across the cylindrical axis of the cell and radial heat transfer only, is confirmed

In all of the well behaved cells examined, the temperature distribution was symmetric, $i e$, no spatial anomalies were observed. As seen in Fig. 4, the temperature is uniform across the major portion of the active electrode area, with the temperature gradients developing toward the center where no active material was present, and toward the outer periphery where the massive stainless steel rings act as an efficient heat sink.

A good estimate of the total heat generated, q, can be obtained from eqn. (1)

$$q = C[E - E(\imath)] \tag{1}$$

TABLE 2

Electrical performance characteristics Li/SOCl$_2$ cells to 2 5 V cutoff

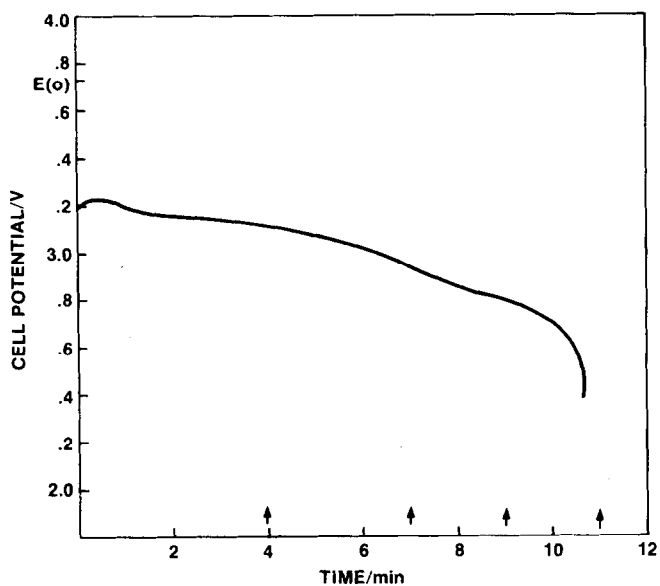| Run time, t^* (min)	Average voltage (V)	Average current (A)	Current density (mA/cm^2)	Capacity (A h)
10 84	3 04	4 07	60 7	0 735
11 72	3 03	4 05	60 5	0 791
8 27	2 95	4 69	70 0	0 646
8 14	3 01	4 78	71 4	0 648
6 53	2 95	5 38	80 3	0 586
6 61	2 99	5 45	81 4	0 600
5 02	2 80	6 25	93 3	0 523
4 19	2 72	6 08	90 7	0 424
4 03	2 77	6 58	98 2	0 443
3 79	2 73	6 65	99 3	0 420

Fig. 3. Typical voltage–time curve for the discharge of an experimental cell. Electrolyte: 1.9M LiAlCl$_4$ + 0.3M AlCl$_3$ in SOCl$_2$; discharge current: 60 mA cm^{-2}; electrolyte: 1.9M LiAlCl$_4$ + 0.3M AlCl$_3$.
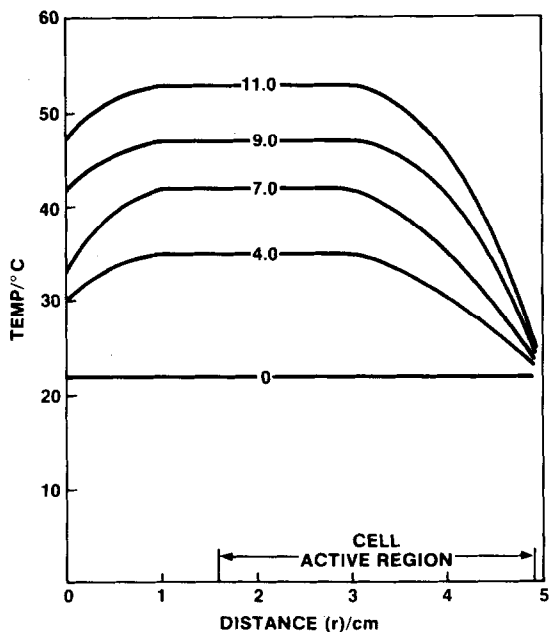

Fig. 4. Evolution of temperature profiles in the discharging Li/SOCl$_2$ cell. Conditions as in Fig. 3.
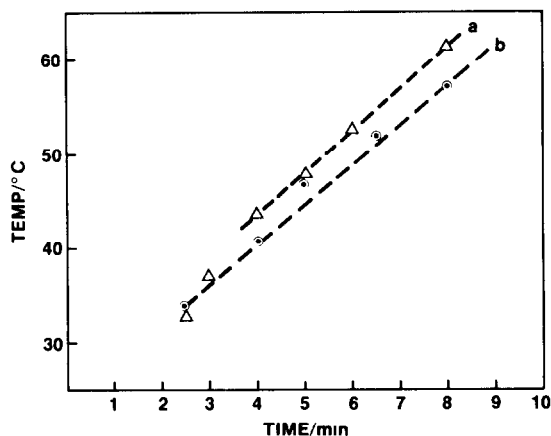
Fig 5 Temperature as a function of discharge time Curve a temperature determined by thermocouple located at active/inactive region (Fig 1) of the central cell of a 10 cell module Curve b temperature determined by liquid crystal film Electrolyte 1 9M LiAlCl$_4$ + 0 3M AlCl$_3$

where E is the thermoneutral potential, $E(i)$ is the average cell voltage, and C is the charge passed in coulombs. With $E = 3.73 \pm 0.04$ V [3] the average heat generation is calculated from the $E(i)$'s listed in Table 2. Since $E(i)$ is only slightly dependent on the discharge current, the total heat generated was essentially the same in all cases, i e , 1690 ± 160 joules. Thus, the plots of the temperature distributions in the cells discharged at different rates are identical if plotted with a scaled time, $\tau = t/t^*$, cf Fig 6.
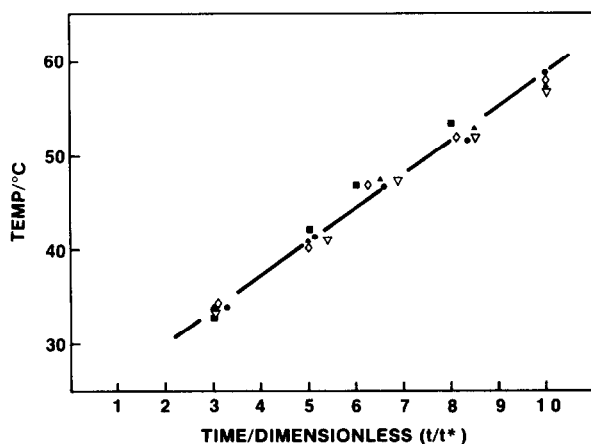

Fig 6 Temperature at the center of active region as a function of scaled time t/t^* Electrolyte 1 9M LiAlCl$_4$ + 0 3M AlCl$_3$ Discharge CD ○, 60 mA cm^{-2}, △, 70 mA cm^{-2}, +, 80 mA cm^{-2}, ●, 90 mA cm^{-2}, □, 100 mA cm^{-2}

Evolution of temperature profiles in defective cells

The defective cells were fabricated with ceramic chips (10^{-4} m dia.) placed at a previously selected point behind the Li anode, here, 2 7 cm from the center line of the cell, *i e* , approximately half way across the center of the electrode active area After the cell was filled with electrolyte and the open circuit potential was established, the external argon pressure was increased which, in turn, decreased the cell spacing so that the Li penetrated the separator and contacted the positive electrode, causing an internal short circuit and therefore a localized heat source. This heat source was so intense that, at the point of contact and in the surrounding area, *ca* 1 cm in diameter, the liquid crystal changes its color from blue to black in less than 1/30 s. Such a change indicates that a temperature well in excess of 120 °C was reached almost instantaneously. The remainder of the cell, except for the periphery, exhibited a temperature of not greater than 60 °C, indicating a quenching of the runaway condition

None of the four cells discharged in this manner ruptured or burned There was a momentary swelling of the cell indicative of a pressure pulse. Because of the slow response of the pressure sensor used, it was not possible to determine its value.

Conclusions

(i)   A method for a complete and time resolved temperature profile in electrochemical cells is described.

(ii)   In well behaved cells, the time dependent temperature distributions are consistent with theoretical predictions.

(iii) In cells with defects leading to internal shorts, this method illustrates their location and the intensity of heat sources

Acknowledgement

References

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