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General safety considerations for high power $Li/SOCl_2$ batteries

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Abstract

Contributions of heat generation and heat management to the internal temperature profile of the $Li/SOCl_2$ cell have been analysed based on thermal modelling. Some approaches are proposed, checked and used in high power $Li/SOCl_2$ cells and batteries, showing improvements in their safety and performance.

Keywords: Safety; Thionyl chloride; Lithium batteries

1. Introduction

$Li/SOCl_2$ battery is an attractive energy source because of its high energy density [1–5]. However, it has been shown from previous results that the high discharge rate and high temperature caused thermal runaway in those cells [6–10]. It was predicted by Marincic [11] for a bipolar $Li/SOCl_2$ battery with 120 kW electrical output that 37.3 kW of heat generated within the 90 kg power source throughout the operation. Meanwhile, electrolyte would boil within 3.5 min, sulfur melt within 5.5 min and lithium melt down within 9.5 min in case of no-forced cooling. Therefore, many searches have dealt with the thermal behaviour of the cells and efforts have been made to develop a safe type of high power $Li/SOCl_2$ cells or batteries.

For example, Dey and Hamilton [12] developed a high rate 'D'-cell and super high-rate (diameter: 3 in, height: <1 in) flat cell [12]. The flat cell delivered 14 Ah on a 100 A continuous drain without any safety problem. In our laboratory, some work have also been done for a better understanding of the thermal behaviour and designing of safe types of high power $Li/SOCl_2$ cells and batteries.

On the basis of thermal modelling of a high power $Li/SOCl_2$ cell with parallel plates [13], heat generation and heat management (including heat absorption and conduction) are two extremely important factors to determine the rate of the increase, the maximum value, and the distribution of the temperature inside the cell during operation.

In this paper, the contributions of heat generation and heat management to the internal temperature profile of the cell have been analysed based on thermal modelling. Some approaches to decrease the heat generation and to improve the heat management in high power $Li/SOCl_2$ cells will be proposed and checked. Finally, safety behaviour improvements have been shown in practical cells and batteries by adopting suitable approaches.

2. Heat generation and heat management versus internal temperature profile of the cell

The same concept of thermal modelling as described in a previous paper [13] has been applied to high power prismatic $Li/SOCl_2$ cell with parallel plates. The heat generation in the cell can be expressed as follows:

$$Q = Q_p + Q_s + Q_f \qquad (1)$$

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

Due to the small contribution of Q_s to Q, Q depends mainly on Q_f and Q_p. Curve (1) and curve (2) in Fig. 1 show calculated internal temperature profiles of prismatic $Li/SOCl_2$ cells with neutral ($LiAlCl_4/SOCl_2$) and acidic ($AlCl_3/SOCl_2$) electrolytes, respectively, based on thermal modelling.

From curve (1) and curve (2) it can be seen that Q_p contributes to the internal temperature profiles. However, there is a significant difference between curve (1) (calculated) and curve (3) (experimental). It indicates that heat generated by corrosion, even in a neutral electrolyte, also shows a certain contribution

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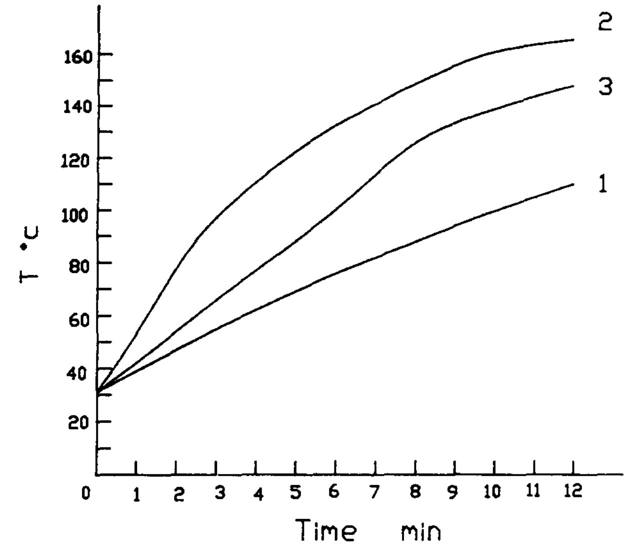

Fig. 1. Internal temperature profiles in different electrolytes: (1) neutral electrolyte ($Q_f = 0$); (2) acid electrolyte, and (3) neutral electrolyte (experimental results). Discharge current density = 35 mA/cm², at ambient temperature.

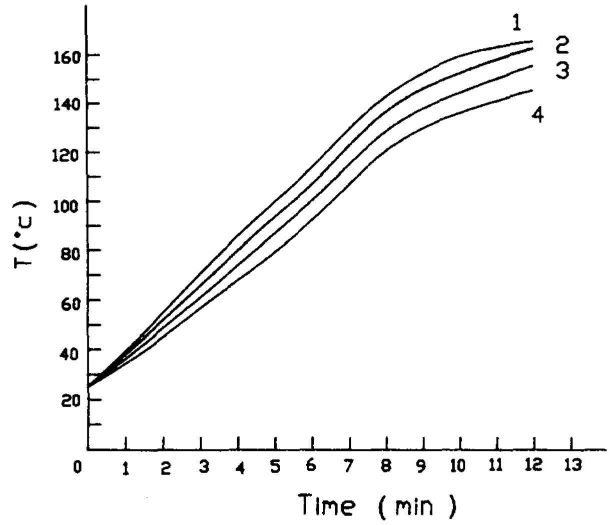

Fig. 2. Effect of working voltage on internal temperature: the working voltages are: (1) 3.0 V; (2) 3.1 V; (3) 3.2 V, and (4) 3.3 V, respectively.

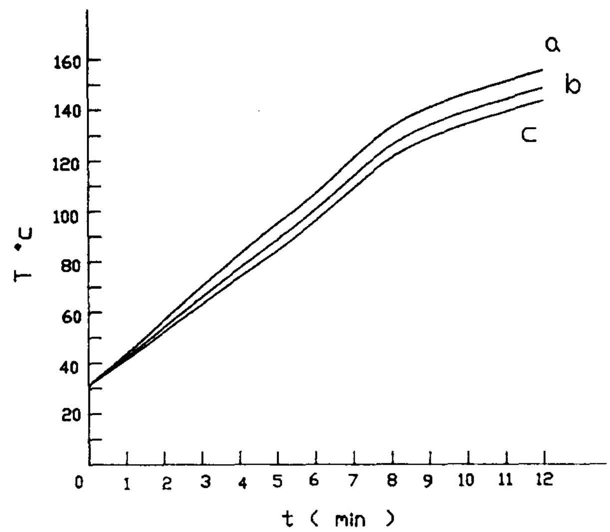

Fig. 3. Effect of different thicknesses of the nickel current collector on the internal temperature: (a) 0.08 mm; (b) 0.12 mm, and (c) 0.15 mm.

to the internal temperature profile. For the understanding of this, some preliminary experiments have been done in our laboratory and the results indicate that lithium shows almost no corrosion in neutral electrolyte at a temperature below 30 °C, but corrosion takes place significantly when temperature goes up to 60 °C [14].

According to:

$$Q_p = I(E_{th} - V) \quad (2)$$

where I is the discharge current, E_{th} the thermoneutral potential of electrochemical system, and V the working voltage. In fact, I is constant for a certain application. Therefore, Q_p depends on the V value.

The internal temperature profiles related to different V values have been calculated based on thermal modelling as shown in Fig. 2. Obviously, the increase in the working voltage can lower rather significantly the heat generated by polarization.

Calculations have been made based on thermal modelling versus the variation of the thickness and weight of each component in the cell. In comparison with the heat generated by polarization or corrosion, the heat management (including heat absorption and conduction) contributed less to the internal temperature profile, if the thickness and weight of the cell have been changed. Among those components (nickel current collector, glass separator, electrolyte, lithium foil, carbon sheet, etc.), the nickel current collector show the greatest effect on heat management, due to its property of high heat capacity and good heat conduction. Fig. 3 shows the effect of different thicknesses of the nickel current collector on the internal temperature.

3. Approaches to decrease the heat generation and to improve the heat management in a high power $Li/SOCl_2$ cell (or battery)

In principle, any approach that can decrease the internal resistance or increase the working voltage of a cell or decrease the corrosion reaction in a cell, may decrease the heat generation during the discharge of a high power $Li/SOCl_2$ cell (or battery). Besides, any approach that can increase heat capacity and heat conduction, may improve the heat management in the cell.

Therefore, the following approaches have been proposed and checked in the Sections 3.1 to 3.6.

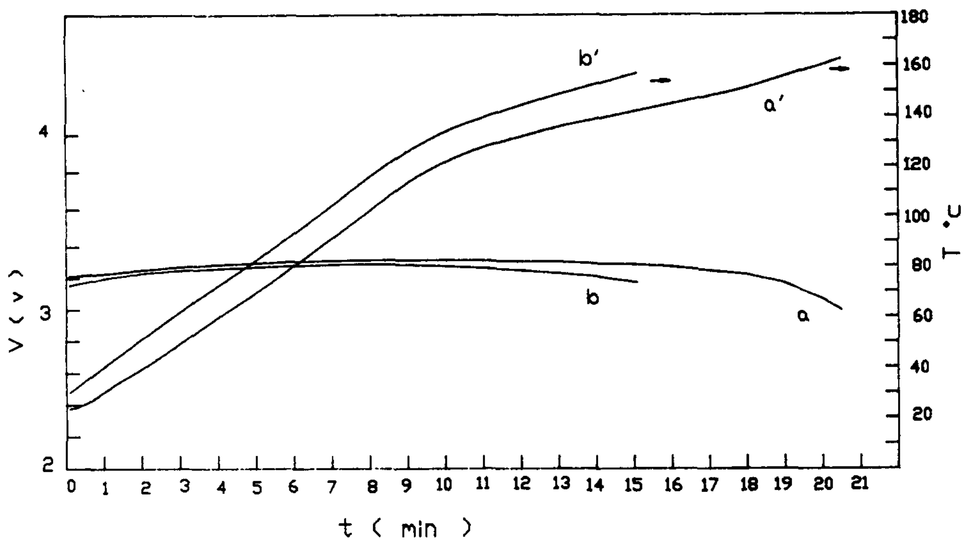

Fig. 4. Discharge characteristics of high power $Li/SOCl_2$ cells with different thicknesses of glass separator: (a, a') 0.12 mm, and (b, b') 0.15 mm. $I = 35$ mA/cm^2.

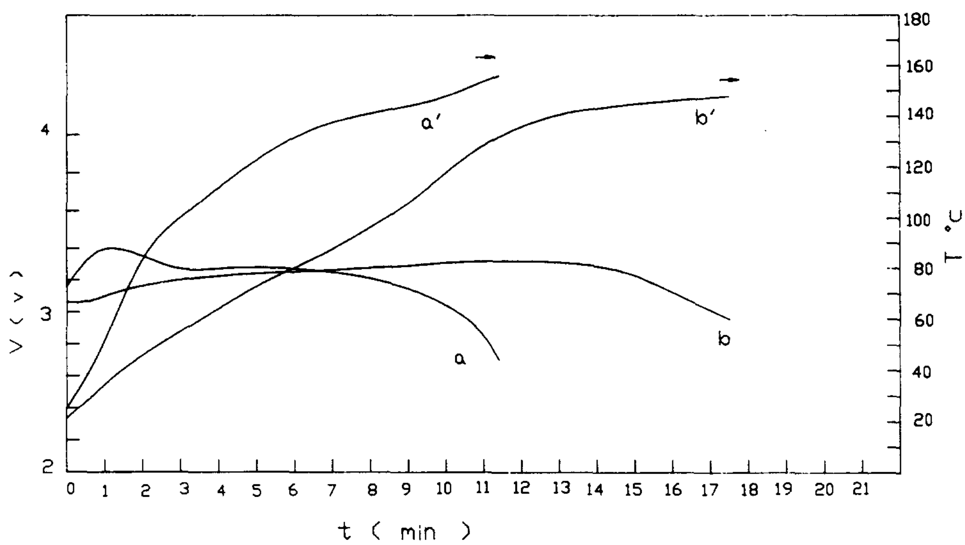

Fig. 5. Discharge characteristics of high power $Li/SOCl_2$ cells with different electrolytes: (a, a') 2.0 M $AlCl_3/SOCl_2$, and (b, b') 2.5 M $LiAlCl_4/SOCl_2$.

3.1. Separators with high saturation of electrolyte, low resistance, no chemical reaction with electrolyte, and enough strength

Glass-fibre separator is a good selection for use in $Li/SOCl_2$ systems, because it features high saturation of electrolyte, stability, enough strength and low resistance in $SOCl_2$-based electrolyte. However, the thickness of the glass-fibre separator shows a great effect on the working voltage of the cell, hence, on the contribution to the temperature profile of the cell, as shown in Fig. 4. Obviously, a thinner glass separator (0.12 mm) is related to a higher working voltage and a lower internal temperature profile. Although a thinner separator (<0.1 mm) may contribute more to the internal temperature profile of the cell than to the discharge characteristics, see Fig. 4, a thin separator may easily cause shortage of the cell.

3.2. Electrolytes with high conductivity and low corrosion reaction against lithium

Fig. 5 shows discharge characteristics of high power $Li/SOCl_2$ cells with different electrolytes. It is seen that although the initial working voltage in this acid electrolyte is higher than that in the neutral electrolyte, the average working voltage and the discharge capacity in the neutral electrolyte is higher than those in the acid electrolyte. In particular, the internal temperature profile in the neutral electrolyte is much lower than that in the acid electrolyte. These results are basically

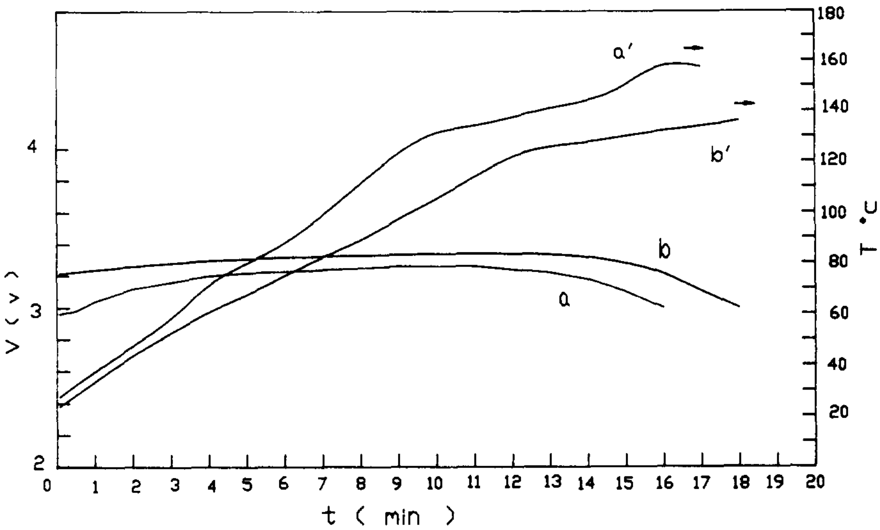

Fig. 6. Influence of a catalyst on the discharge characteristics of high power $Li/SOCl_2$ cells at 20 °C: (a, a') without catalyst, and (b, b') with catalyst. $I = 35$ mA/cm^2.

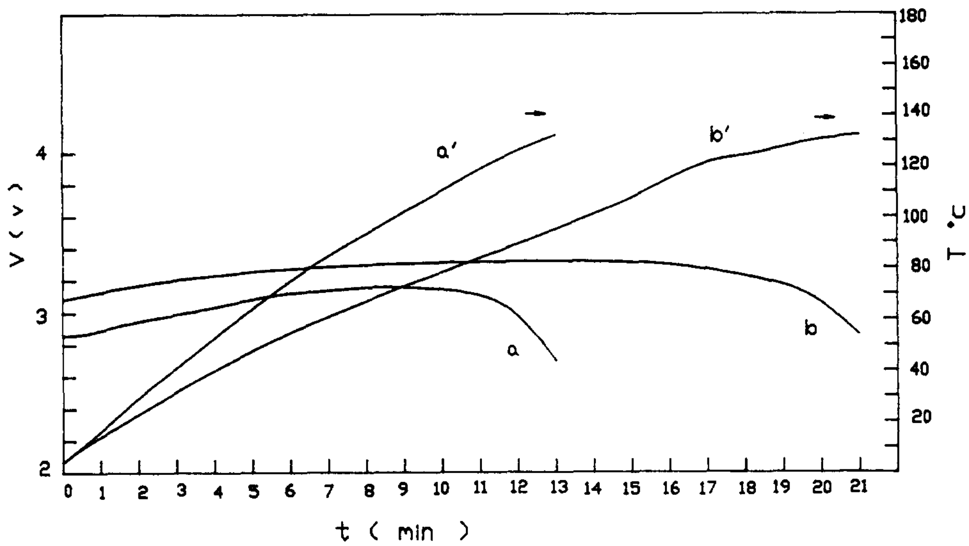

Fig. 7. Influence of a catalyst on the discharge characteristics of high power $Li/SOCl_2$ cells at 0 °C: (a, a') without catalyst, and (b, b') with catalyst. $I = 35$ mA/cm^2.

consistent with those calculated and based on thermal modelling (Fig. 1).

A selection of suitable concentrations of $LiAlCl_4/SOCl_2$ has also been made experimentally. It indicates that 2.5 $LiAlCl_4$ is suitable in high power $Li/SOCl_2$ cells, due to its higher conductivity, higher solubility in reaction products, and lower reaction activity with lithium.

3.3. Catalysts increasing the working voltage, lowering the internal pressure and improving low temperature performance of the cell

Several catalysts have been tested in $Li/SOCl_2$ cells with a neutral electrolyte. Fig. 6 shows the influence of a catalyst on discharge characteristics of high power $Li/SOCl_2$ cell at 20 °C. Obviously, the average working voltage with catalyst is >100 mV higher than that without catalyst and the internal temperature profile with catalyst (Fe–TAP) is lower than that without catalyst. Besides, the low temperature performance of high power $Li/SOCl_2$ cell shows significant improvement using a catalyst, see Fig. 7. The catalyst played also an important role in reducing the internal pressure of the cell [15].

3.4. Current collectors with a lower resistance

As calculated above, experiments have also shown that the thicker nickel current collector can improve the heat management, hence, lower the internal temperature profile of the cell, as shown in Fig. 8. Although copper has a higher heat conduction rate and a higher conductivity, the effect on the internal temperature profile is not very obvious.

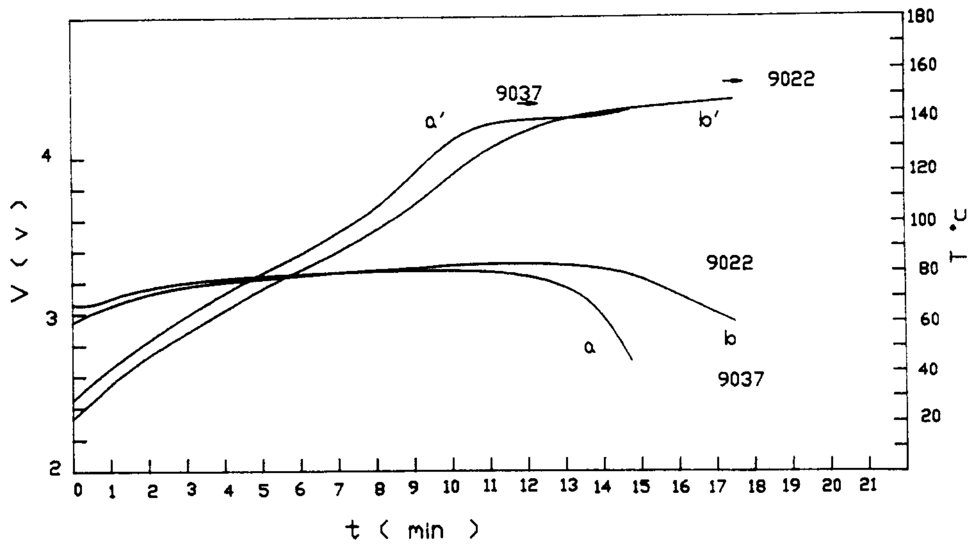

Fig. 8. Discharge characteristics of high power Li/$SOCl_2$ cells with different thicknesses of the nickel current collector: (a, a') 0.10 mm, and (b, b') 0.15 mm.

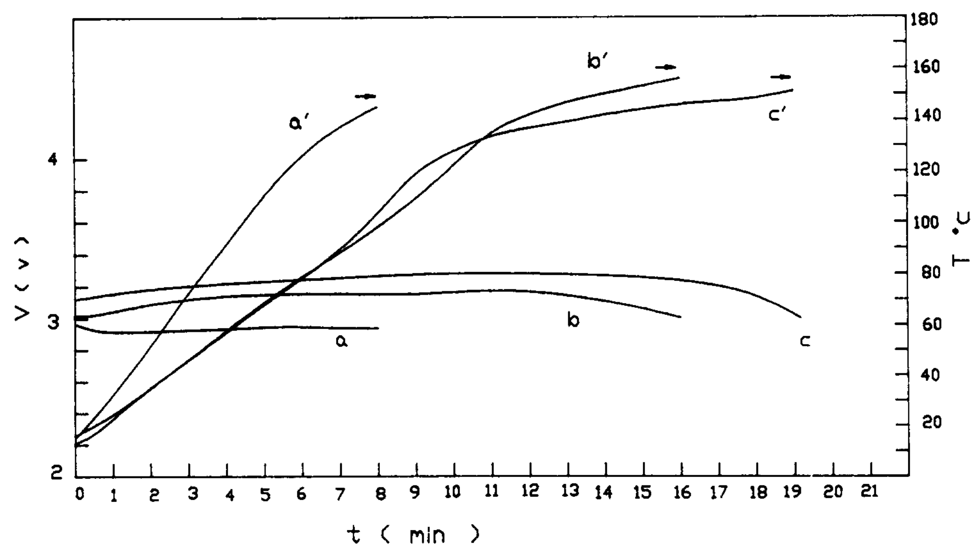

Fig. 9. Influence of different cell terminals on the discharge characteristics of high power Li/$SOCl_2$ cells: (a, a') aluminium terminal; (b, b') copper terminal, and (c, c') modified copper terminal.

3.5. Terminal materials structures

Due to very high current through the terminals and all the contacts which are between electrode and current collectors, and between current collectors and terminals in a high power Li/$SOCl_2$ cell, it is extremely important to select suitable materials and optimum technology for making these terminals and contacts with lower resistance, high heat conduction and heat capacity. Fig. 9 shows the influence of different cell terminals on the discharge characteristics of high power Li/$SOCl_2$ cells. Obviously, the copper terminal is much better than the aluminium terminal used in the cell, the modified copper terminal shows a further improvement in discharge characteristics of the cell.

3.6. Tightness of electrode groups

The tightness of electrode groups inside cell container has a great relation with cell internal resistance. Control of a suitable tightness of assembling the electrode groups inside a cell container can give a lower resistance of the cell, hence, improve the discharge characteristics of the cell. Fig. 10 indicates that the approach is effective. Besides, some approaches to increase the heat capacity and heat conduction of the cell components can be adopted, a phase change material can be also used to absorb much of the heat transferred from cells and keep the temperature of the medium at a lower value (around phase change temperature).

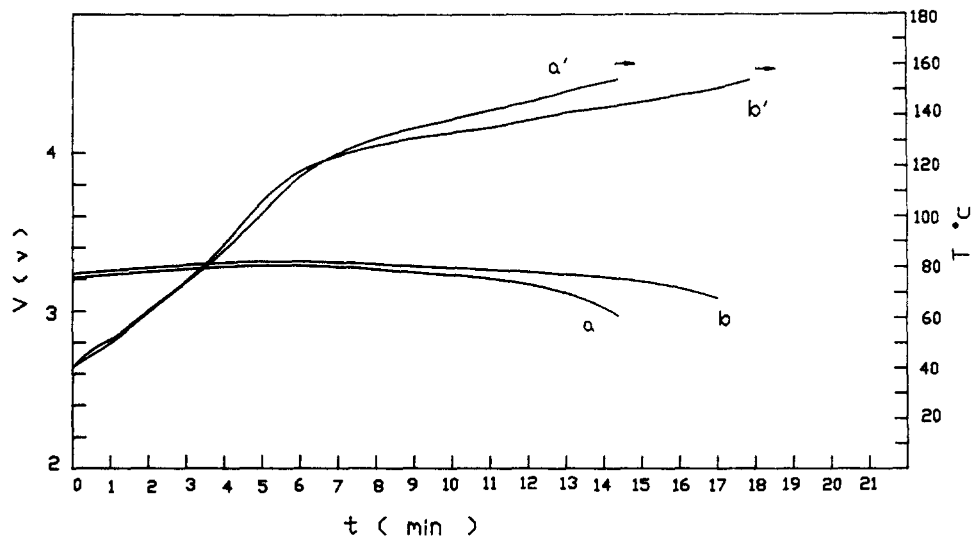

Fig. 10. Discharge characteristics of high power Li/$SOCl_2$ cells with different tightnesses of assembling electrode groups inside the container: (a, a') 93%, and (b, b') 97%.

4. Safety behaviour improvements shown in practical cells and batteries

Fig. 11 shows some typical discharge curves and temperature profiles of three batteries consisting of 6, 12 and 24 high power prismatic cells in series, respectively. The total output power of above batteries is about 16, 32 and 64 kW, respectively. Those cells are made by adopting all the approaches mentioned above. It is seen from Fig. 11 that the average voltage of a cell is about 3.2 V and the highest temperature values in the centre of a cell are the same among the three batteries (around 140 °C by end of 12 min). It indicates that high power Li/$SOCl_2$ batteries designed and produced in our laboratory show a very good performance and safe behaviour. Also, another practical battery consisting of 40 'D'-size spiral-wound Li/$SOCl_2$ cells in series and parallel can delivery over 600 W of power. However, it can only operate continuously for 30 min without any safety problem. A phase change material selected is used inside battery container and a significant improvement in the temperature profile makes that discharge time increases from 30 min to more than 45 min even at 50 °C without any safety problem. Figs. 12 and 13 show typical discharge characteristics of such batteries.

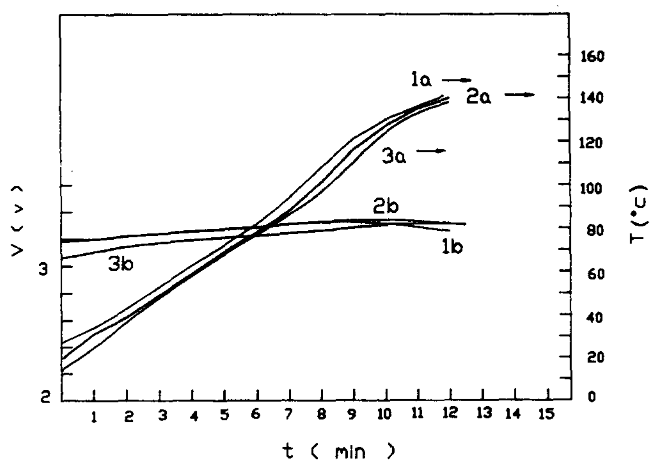

Fig. 11. Typical discharge curves and internal temperature profiles of high power Li/$SOCl_2$ batteries: (1a) one cell in 16 kW batteries; (2a) one cell in 32 kW batteries; (3a) one cell in 64 kW batteries; (1b) one cell in 16 kW batteries; (2b) one cell in 32 kW batteries, and (3b) one cell in 64 kW batteries.

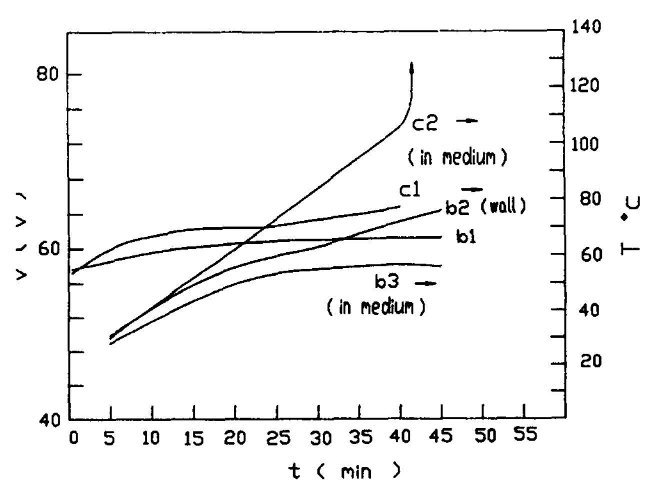

Fig. 12. Influence of PCM on discharge characteristics of batteries at 25 °C: (b1, b2, b3) with PCM, and (c1, c2) without PCM. I = 10 A. (b1, c) = voltage; (b2, b3, c2) = temperature.

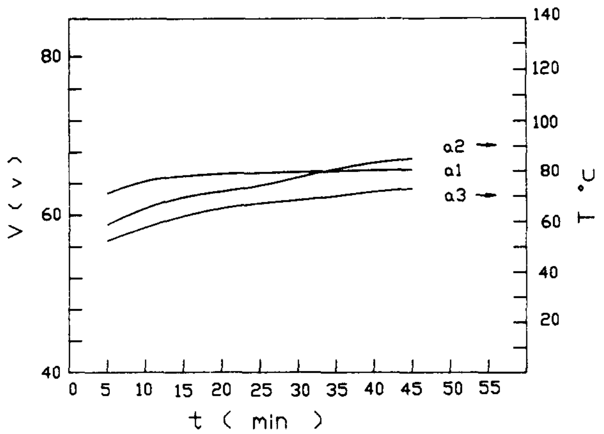

Fig. 13. Discharge characteristics of batteries with PCM at 50 °C: (a2) wall temperature, (a3) in, and (a1) = voltage.

5. Conclusions

1. Based on thermal modelling heat generation and heat management are two factors determining the internal temperature profile of the high power $Li/SOCl_2$ cells.

2. Some approaches to decrease heat generation and to improve heat management in a high power $Li/SOCl_2$ cell (or battery) have been proposed and checked.

3. Safety improvements have been shown in several types of high power $Li/SOCl_2$ cells and batteries by adopting these approaches.

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