

Li/SOCl₂ CELLS FOR HIGH TEMPERATURE APPLICATIONS

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Summary

The capacity of Li/SOCl₂ cells operating at temperatures as high as 150 °C has been measured at discharge rates up to 5 mA/cm². The results indicate the unique chemical and electrochemical stability of the system, manifested by its ability to be discharged continuously at 150 °C for more than 2 months while obtaining 70% of the cell nominal capacity.

The capacity-temperature plot shows a maximum at 50 °C. Above 50 °C the capacity decreases as a result of the increase in the self-discharge current at higher temperature. An anomalous capacity increase is found at temperatures above 100 °C. Above this temperature it has been shown that thermal decomposition products may increase the cathodic reaction rate and modify the structure of the passivation layer on the anode surface. Over the 100 - 150 °C temperature range the lithium chloride film morphology, as analysed by SEM, tends to be of a smaller crystal size the higher the temperature. This trend is in opposition to that found at the lower temperature range, *e.g.*, -40 to 70 °C. In addition, the decomposition product, *e.g.*, SO₂, improves the transport properties of the electrolyte and thus increases the carbon cathode efficiency.

Introduction

One of the promising normal temperature lithium systems selected for commercialization in recent years utilizes the lithium-thionyl chloride couple. This system is characterized by its high gravimetric and volumetric energy densities (in excess of 400 Wh/kg and 850 mWh/cm³), good operating capabilities over a wide temperature range, reasonably high current delivering capabilities, and low self-discharge rates.

The unique feature of the system is that one component, thionyl chloride, serves the dual role of electrolyte carrier for the solute ions, as well as being the active depolarizer. The absence of organic solvent is reflected by an enhancement of both the chemical and the electrochemical stabilities of the Li/SOCl₂ system. Using differential thermal analysis (DTA) measurements it was shown [1] that the instability of organic lithium batteries is determined

by the tendency to thermal runaway, initiated by the exothermic reaction between the lithium anode and the organic electrolyte.

The chemical stability of the Li/LiAlCl₄, SOCl₂/C system as demonstrated by storage at temperatures of 170 - 190 °C for 24 h [2], and the electrochemical stability as manifested by the capability of the system to be discharged at temperatures as high as 150 °C [2], suggested that the operating temperature range can be extended to at least 150 °C. In the present communication we report results on the performance of Li/SOCl₂ cells at elevated temperatures and discuss the morphology of the passivation film grown on the surface of lithium metal immersed in 1.8M LiAlCl₄ in thionyl chloride at temperatures up to 150 °C (for comparison, the boiling point of thionyl chloride is 79 °C).

Experimental

The electrical discharge measurements were conducted on D size cells, with a "bobbin" carbon cathode configuration [3, 4]. These cells were designed for low rate applications by limiting the apparent electrode surface area. The surface area of the lithium anode was 45 cm². The nominal capacity of these cells is 10 A h at discharge rates of 1.5 mA/cm² at 20 °C. The basic materials and construction of these cells have been described elsewhere [4]. At least three cells were taken for each measurement.

The lithium specimens for scanning electron microscope (SEM) examination, mounted on a nickel disc, were stored with electrolyte (1.8M LiAlCl₄ in thionyl chloride) in a hermetically sealed cell which contained additional lithium cell foil swaged against the nickel plated, cold-rolled steel can to reduce possible hardware corrosion, as shown schematically in Fig. 1. The need for a metallic container stemmed from the high pressure of up to 30 atm expected for the vapor pressure of 1.8M LiAlCl₄ in thionyl chloride at storage temperatures ranging from 120 to 150 °C.

After a specified period of storage, the upper part of the metallic container was cut and the specimens were thoroughly rinsed in LiCl-saturated, distilled thionyl chloride, and dried. They were carried in a dry container to the SEM site. The specimens were loaded in the SEM with the aid of an argon-filled glove bag which was attached to the SEM port.

Results

Figure 2 shows typical low rate discharge curves at 150 °C, *e.g.*, 0.1 - 0.5 mA/cm². At the lowest rate, which lasted over two months of discharge, the nominal capacity was reduced by approximately 30%. This degree of electrochemical stability, which is unique to the Li/SOCl₂ system, will be discussed further later in this work. For higher discharge rates, *e.g.*, up to 5 mA/cm², most of the available capacity was obtained independent of the

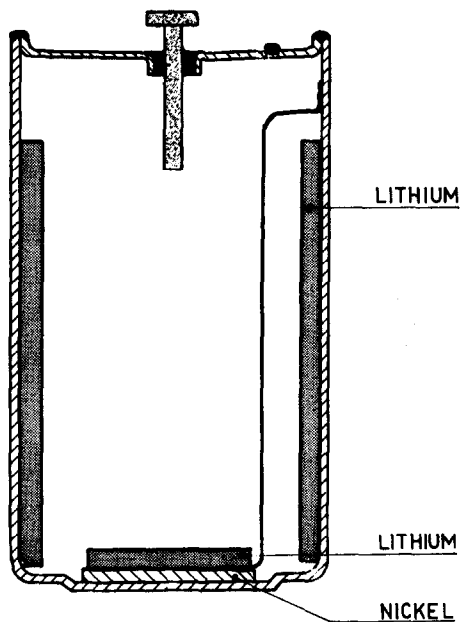


Fig. 1. Cross sectional view of hermetically sealed metallic container for the elevated temperature storage of lithium specimens for SEM.

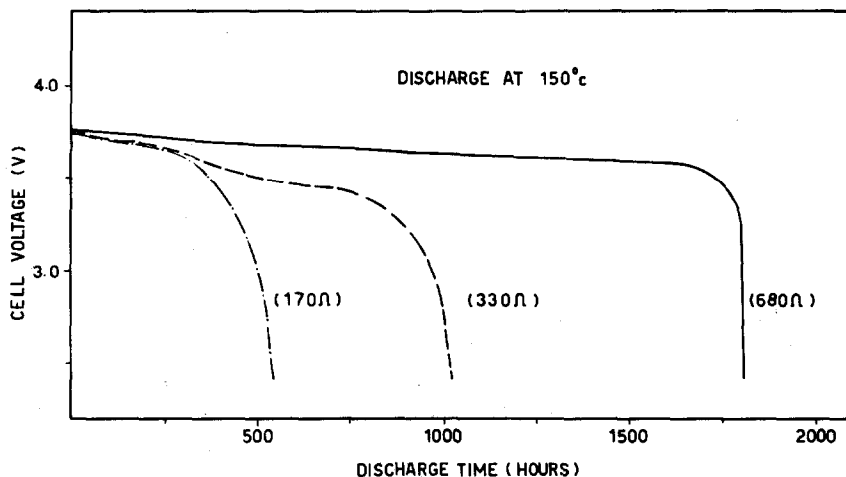


Fig. 2. Discharge characteristics of D size Li/SOCl₂ cell at three constant loads at 150 °C.

discharge current. Figure 3 summarizes the capacities obtained at discharge rates ranging from 0.1 to 5 mA/cm² at 150 °C.

The temperature characteristics of D size Li/SOCl₂ cells obtained at two discharge rates of 1.5 mA/cm² and 3 mA/cm² are shown in Fig. 4. For the lower rate more than 75% of the nominal capacity is obtained over most of the temperature range, *e.g.*, -20 - 150 °C, while for the higher rate this frac-

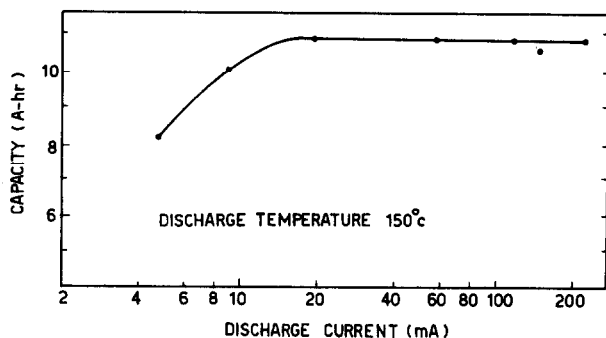


Fig. 3. The effect of discharge rate on the capacity of D size Li/SOCl₂ cells discharged at 150 °C.

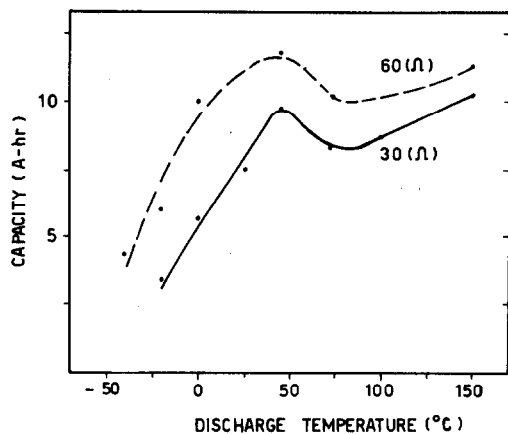
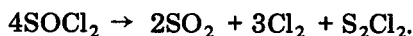


Fig. 4. Discharge capacities as a function of discharge temperature at 1.5 mA/cm² and 3 mA/cm².

tion is obtained from 30 to 150 °C. The capacity decrease at the lowest temperature range is caused by preferential blockage of that side of the cathode facing the anode [4, 5]. The conductivity increase and the lowering of the electrolyte viscosity at higher temperatures increase the carbon cathode reduction reaction efficiency. Thus the capacity reaches a maximum at 50 °C. The capacity decrease at higher temperatures is expected on the grounds of increasing self-discharge currents [4]. The anomalous capacity increase found for the highest temperature range may be caused by partial decomposition of the thionyl chloride to give electroactive products, this taking place at temperatures above 100 °C [6]. The presence of the high surface area carbon current collector seems to increase the decomposition rate.

The accepted decomposition equation is [6]:



The presence of the electroactive decomposition products in the cell electrolyte could give rise to the anomalous capacity increase as a result of

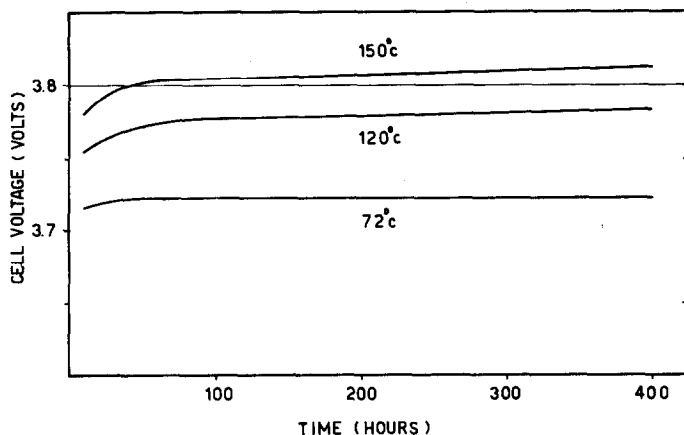


Fig. 5. The change of cell open circuit potentials with storage time at 72, 120, and 150 °C.

the increase of the reduction rate, by the modification of the nature of the passivation layer on the lithium anode, and by improving the transport properties of the electrolyte.

The value of the open circuit potential (OCV) of cells may be indicative of the formation of new electroactive species. Figure 5 shows that the OCV values of cells experience a gradual increase with time during storage at 120 °C and 150 °C, while the OCV value for cells stored at 72 °C is relatively stable. The gradual increase in OCV may indicate the formation of new species with higher reduction potentials than thionyl chloride. The OCV of cells which were kept at room temperature following storage at 120 °C or 150 °C does not decrease to the initial cell voltage but maintains a high value. Typical behaviour of the OCV values of cells at the end of two days storage at 120 °C and 150 °C, and the OCV values of the same cells after 45 days further storage at room temperature, are given in Table 1.

For comparison Table 1 includes the OCV values of the cells at room temperature prior to the high temperature storage. The results given in the

TABLE 1

The influence of room temperature (RT) storage preceded by 2 days storage at 120 °C and 150 °C on the OCV of cells. For comparison the OCV of cells stored at RT is given. Each value is the average from 4 cells.

Storage conditions	O.C. potential (mV)
RT	3670 ± 2
2 days 120 °C	3773 ± 3
2 days 120 °C + 45 days RT	3802 ± 2
2 days 150 °C	3801 ± 3
2 days 150 °C + 45 days RT	3838 ± 3

Table indicate that the decomposition species formed at temperatures above 100 °C is a stable compound, probably chlorine, since addition of 20% S_2Cl_2 to 1.8M $LiAlCl_4$ in $SOCl_2$ does not increase the OCV of the cell, while 5% of Cl_2 increases the OCV to 3.9 V.

The influence of the storage temperature on the morphology of the passivating layer of the lithium anode has been reported in the literature [7, 8]. It is found that the higher the temperature the thicker the layer, the larger the $LiCl$ crystals in the outermost surface of film facing the electrolyte, and the greater the porosity of the layer. These trends can be seen in Fig. 6 which shows SEM photographs of lithium specimens stored at room temperature and at 72 °C for 40 days.

On the other hand, the surface morphology of lithium anodes stored at 120 °C and 150 °C does not comply with this trend. Figure 7 shows that after 7 days storage at 120 °C the particle size of lithium chloride crystals is larger than that at 72 °C, while storage at 150 °C yields an average particle size lower than that found at 120 °C and 72 °C. At 120 °C less than 0.3% of the surface film is covered by giant crystals of approximately 100 μm dimension, as can be seen in Fig. 7. These large crystals were not found on samples stored at 150 °C. The anode surface morphology at temperatures higher than 150 °C is currently under investigation.

The decrease of the crystal size found at 150 °C can be the result of the influence of the increased SO_2 content in the electrolyte due to thionyl chloride decomposition. It has been shown by Dey [1, 7] that the presence of sulfur dioxide in the electrolyte reduces the size of the lithium chloride crystals.

In addition, the presence of sulfur dioxide in the electrolyte increases its conductivity and reduces its viscosity [8]. Thus, the presence of sulfur dioxide improves the transport properties of the electrolyte in the carbon cathode pores, and thus increases its efficiency toward the reduction of thionyl chloride.

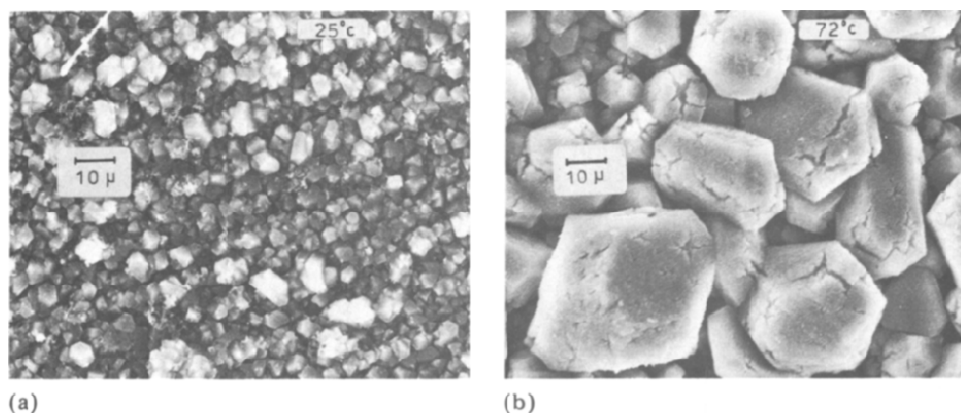


Fig. 6. SEM photographs of Li surface exposed to 1.8M $LiAlCl_4-SOCl_2$ for 40 days at (a) 25 °C and (b) 72 °C. (Magnification $\times 540$.)

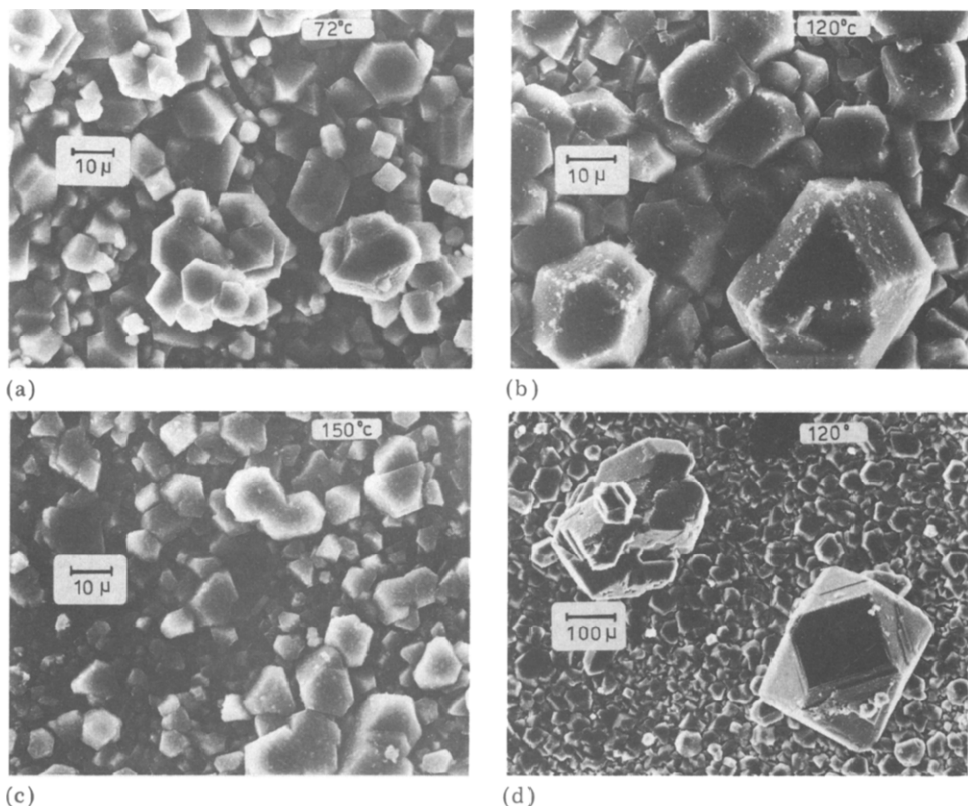


Fig. 7. SEM photographs of Li surface exposed to 1.8M $\text{LiAlCl}_4\text{-SOCl}_2$ for 7 days (a) at 72 °C, (b) at 120 °C, (c) at 150 °C, (d) at 120 °C showing large crystal growth. (Magnification (a), (b), (c) $\times 540$, (d) $\times 130$.)

The porosity of the films at these high temperatures can be seen in the SEM photographs at higher enlargements. Figure 8 shows a typical pore structure in lithium chloride films grown at 150 °C ($\times 2700$ magnification).

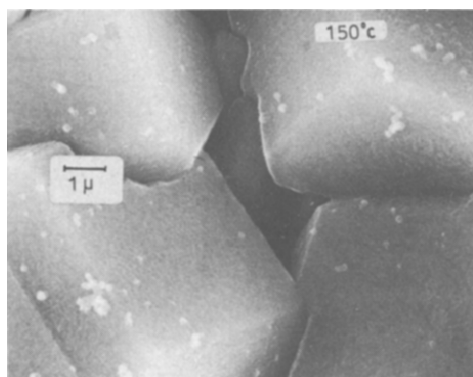


Fig. 8. SEM photographs of Li surface exposed to 1.8M $\text{LiAlCl}_4\text{-SOCl}_2$ for 7 days at 150 °C, showing typical pore structure. (Magnification $\times 2700$.)

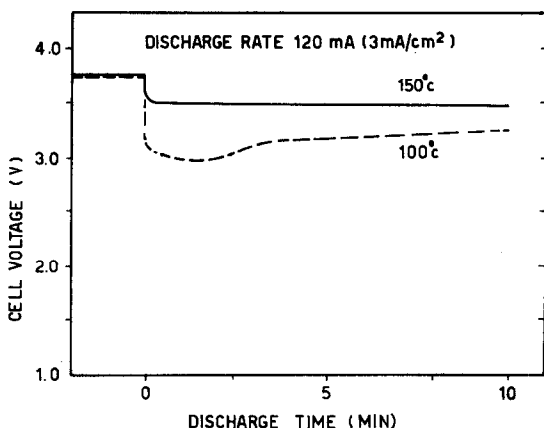


Fig. 9. The voltage delay in Li/SOCl₂ D-size cells after 1 year's storage at room temperature, at 3 mA/cm² load at 150 °C and 100 °C.

The porosity of the film can be deduced also from the behaviour of the cell voltage drop from its OCV value on the first application of a load (voltage delay behaviour). Figure 9 shows typical results of cells stored for 1 year at room temperature and then thermally equilibrated for 12 - 16 h at high temperature.

At 150 °C the voltage level always stabilized (instantly on first application of a load) at the plateau level; at 100 °C the voltage may drop to 3 V and then recover to the normal working voltage. For both temperatures the cells exhibit no voltage delay to 3 V.

These voltage delay results indicate that even though the crystals are smaller at 150 °C than at 100 °C the porosity of the film is higher.

The low self-discharge rate observed for the Li/SOCl₂ couple at temperatures up to 150 °C, as shown at the lowest discharge rate in Fig. 3, is in agreement with earlier findings at 72 °C [9, 10]. Figure 10 shows the capacity reduction as a result of long term storage at 55 °C and at 70 °C with, and without, 1.5 μA/cm² continuous discharge current. It can be seen that the capacity reduction levelled off after 3 - 6 months storage, and practically no further capacity reduction can be observed for up to 15 months storage at these temperatures. In addition, the relatively weak dependence of the capacity retention on the storage temperature (55 °C and 70 °C) is in agreement with earlier results [7] on the dependence of film thickness on storage duration. The experimental evidence that the passivation film formed on the lithium at 150 °C is more porous than that formed at lower temperature, although self discharge at the higher temperatures remains small, implies that the porous film seen in the SEM photographs is not the only film present, but that there is also present an underlying, non-porous passivating film that controls the self discharge rate and, accordingly, the stability of the system. This duplex film model was suggested recently by Moshtev *et al.* [11], and by Peled and Yamin [12], who proposes that the passivation layer on the lithium anode consists of a thin film of dense, insulating LiCl of several molec-

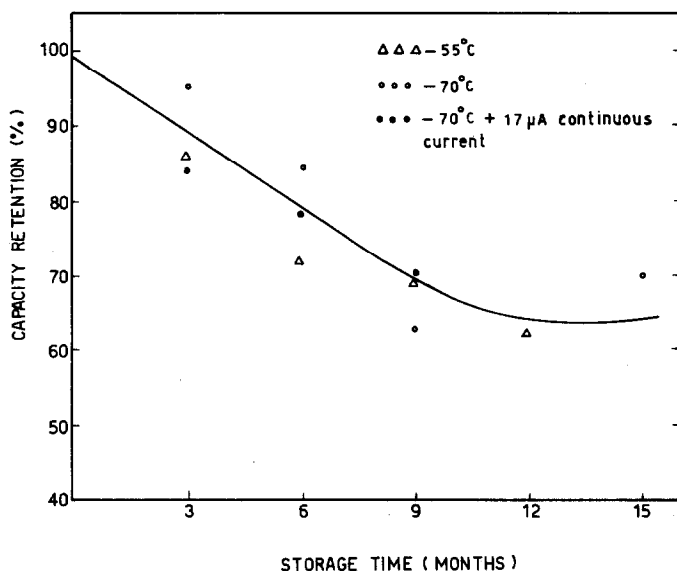


Fig. 10. Capacity retention of Li/SOCl₂ AA size cells following storage at 55 °C and 70 °C with, and without, continuous discharge current of 1.5 μA/cm².

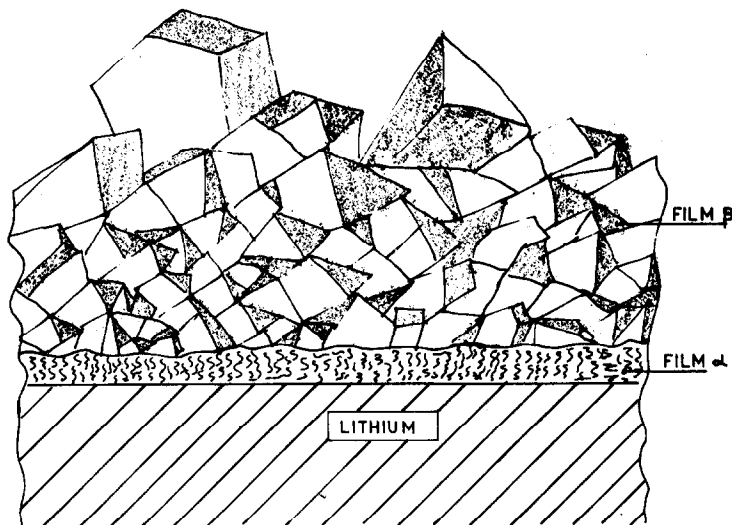


Fig. 11. A schematic cross sectional view of the model suggested for the passivation film on the lithium anode.

ular layers (film α) underlying a thicker layer of porous, non-insulating LiCl film which may reach 100 μm in thickness (film β). The levelling off of the thickness of the compact layer governs the self-discharge current, and the electrochemical stability of the system. A schematic representation of the passivating layer structure is shown in Fig. 11.

It should be noted that in the limiting case, film α may have a minimal thickness, and in this case the stability of the lithium is of a kinetic nature. The stability of lithium metal encountered in a large variety of chemical environments (solid-gas and solid-liquid) leads us to favor the kinetic model to account for the unique stability of the lithium metal. The presence of water in a lithium-gas interface, and organic solvent in a lithium-liquid interface, reduces the stability, as a result of the formation of unprotective surface layers.

Conclusions

The development of cylindrical Li/SOCl₂ cells for high temperature applications has expanded the temperature span of this system from below -40 °C to 150 °C. For externally unheated cells this temperature range is the widest known to date. For most of the range, at least 75% of the nominal capacity was obtained for discharge rates of 1.5 and 3 mA/cm².

The extreme electrochemical and chemical stability of the Li/SOCl₂ system is manifested by its capability to be discharged continuously for more than 2 months at 150 °C while still yielding 70% of the nominal capacity.

The thermal decomposition of thionyl chloride at temperatures above 100 °C probably yields chlorine, sulfur monochloride, and sulfur dioxide. The products have no adverse effect on the battery performance since they increase the cathodic rate capability, decrease the self discharge as a result of decrease in the crystal size of the passivation layer on the lithium anode, and increase the carbon cathode efficiency. These products may also be responsible for the anomalous capacity increase found at temperatures above 100 °C, which is contrary to the expected capacity decrease on the grounds of the increased self-discharge at higher temperatures.

The absence of organic solvent as an electrolyte was suggested as the reason for the unique stability of the Li/SOCl₂ couple.

A double film model for the anode passivation layer is suggested as an explanation of the results obtained in this work.

Acknowledgement

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References

- 1 A. N. Dey, *Proc. Workshop on Lithium Nonaqueous Battery Electrochemistry, June 4 - 6, 1980*, The Electrochemical Society Inc., Princeton, NJ, p. 83.

- 2 M. Babai and U. Zak, *Proc. 29th Power Sources Symp., Atlantic City, NJ, 1980*, p. 150.
- 3 J. J. Auburn and N. Marincic, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, New York, 1975, p. 683.
- 4 Tadiran Lithium Inorganic Batteries, *Tech. Rep., LBR-1507*, Nov. 1981.
- 5 A. N. Dey and P. Bro, *J. Electrochem. Soc.*, 125 (1978) 1574.
- 6 R. Cherton, *Bull. Soc. Roy. Sci., Liège*, 11 (1942) 54.
- 7 A. N. Dey, *Thin Solid Films*, 43 (1977) 131.
- 8 Unpublished results.
- 9 D. Morley and R. J. Solar, *Proc. 28th Power Sources Symp., Atlantic City, NJ, 1978*, The Electrochem. Soc. Inc., NJ, USA, p. 232.
- 10 Y. Gal, M. Babai and U. Zak, Abstr. 36.16, *Proc. 12th Int. Conf. on Medical and Biological Engineering, Jerusalem, Israel, August 19 - 24, 1979*, The Electrochem. Soc. Inc., NJ, USA.
- 11 R. V. Moshtev, Y. Geronov and B. Pureshev, *J. Electrochem. Soc.*, 128 (1981) 1851.
- 12 E. Peled and H. Yamin, *Proc. 27th Power Sources Symp., Atlantic City, NJ, 1976*, The Electrochem. Soc. Inc., NJ, USA, p. 237.