REACTION PRODUCTS ON CURRENT OR POTENTIAL REVERSAL IN Li/SOCl$_2$ CELLS

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Summary

The products formed during abnormal operation due to current or potential reversal in Li/SOCl$_2$ cells have been identified by several complementary analytical techniques. In addition to the expected corrosion of cell components, the following compounds were found: Cl$_2$, SO$_2$, SO$_2$Cl$_2$, S$_2$Cl$_2$ and SCl$_2$. The presence of Cl$_2$O and ClO$_2$, reported earlier by others, has not been confirmed.

Introduction

Uncontrolled and often violent events have occasionally occurred during the development phase of the high energy density, high discharge rate, reserve Li/SOCl$_2$ battery. These events can take place at any time after the introduction of the electrolyte, *i.e.*, during the battery activation, during the discharge, as well as during the post-discharge period. Such behavior is not unexpected inasmuch as this system is (i) highly energetic (with the energy density approaching that of an explosive) and (ii) in a state capable of spontaneous reaction.

The most common cause of the initiation of an uncontrolled event is the development of excessive temperatures, either throughout the battery volume [1] or through the formation of local hot spots. A further suggested cause for the development of violent behavior is a chemical reaction involving cell components and triggered by the presence of highly reactive intermediates. Specifically, it was suggested that these unstable species could be generated during normal operation of the battery [2], during the forced overdischarge, and during the charging process [3].

In regard to safety issues related to a normal operation, it was proposed a few years ago that discharge reaction in neutral electrolytes may constitute a hazard due to the accumulation of highly energetic SO-molecules. However,

subsequent work [4, 5] has failed to confirm their presence. Similarly, controversy existed as to whether or not hazardous species, *e.g.*, Cl_2O, ClO_2, are generated under abnormal conditions, *i.e.*, on oxidation of an acid electrolyte [3].

This communication discusses the changes in the composition of the electrolyte phase resulting from abnormal operating conditions, and assesses the probability of chemical causes originating these uncontrolled and, at times, violent behaviors of $Li/SOCl_2$ cells.

Experimental

Electrochemical cells. Three types of electrochemical cells, shown in Fig. 1(a) - (c), were constructed and assembled in a dry box under positive argon pressure. A single compartment cell, Fig. 1(a), was used to simulate conditions in a battery where reaction products generated at the positive electrode can diffuse to the negative electrode and subsequently undergo reduction. A three compartment cell, Fig. 1(b), provided with a sampling port, was designed for quantitative work. Figure 1(c) shows the construction of a cell designed for rapid collection of oxidation products used in electron spin resonance (ESR) measurements. In this cell, a thin layer of the electrolyte flows over the anode and drops into the collection vessel which is cooled to −100 °C.

Electrodes. Carbon electrodes were prepared by applying a 10% Teflon−Shawinigan black mix to an expanded nickel metal, followed by rolling, drying, and sintering the electrode at 280 °C.

Chemicals. Thionyl chloride (Aldrich Co.) was vacuum distilled from triphenylphosphite. Lithium chloride (Alfa Co.) was dried under vacuum at 130 °C for 24 h prior to use. Aluminum chloride (Fluke AG, puriss.) was used as received.

Apparatus. Forced overdischarge of experimental cells was carried out with an Electronic Measurements, Model C629, constant power supply. A Fluke, Model 8021 B multimeter and a Hewlett Packard, Model 7132 A recorder monitored the cell current and potential, respectively.

Five analytical techniques were employed to identify the compounds produced during forced overdischarge of the cell. These were:

(i) gas chromatography (Hewlett-Packard, Model 5880 GC, with a 6 foot, 0.25 in. glass column packed with 10% QF-1 on 80/100 chromosorb G);

(ii) atomic absorption spectroscopy (Perkin Elmer, Model 303 spectrometer);

(iii) electron spin resonance spectroscopy (Varian E-line Century spectrometer, operating at X-band frequency of 9.1 - 9.5 GHz and employing 100 kHz modulation);
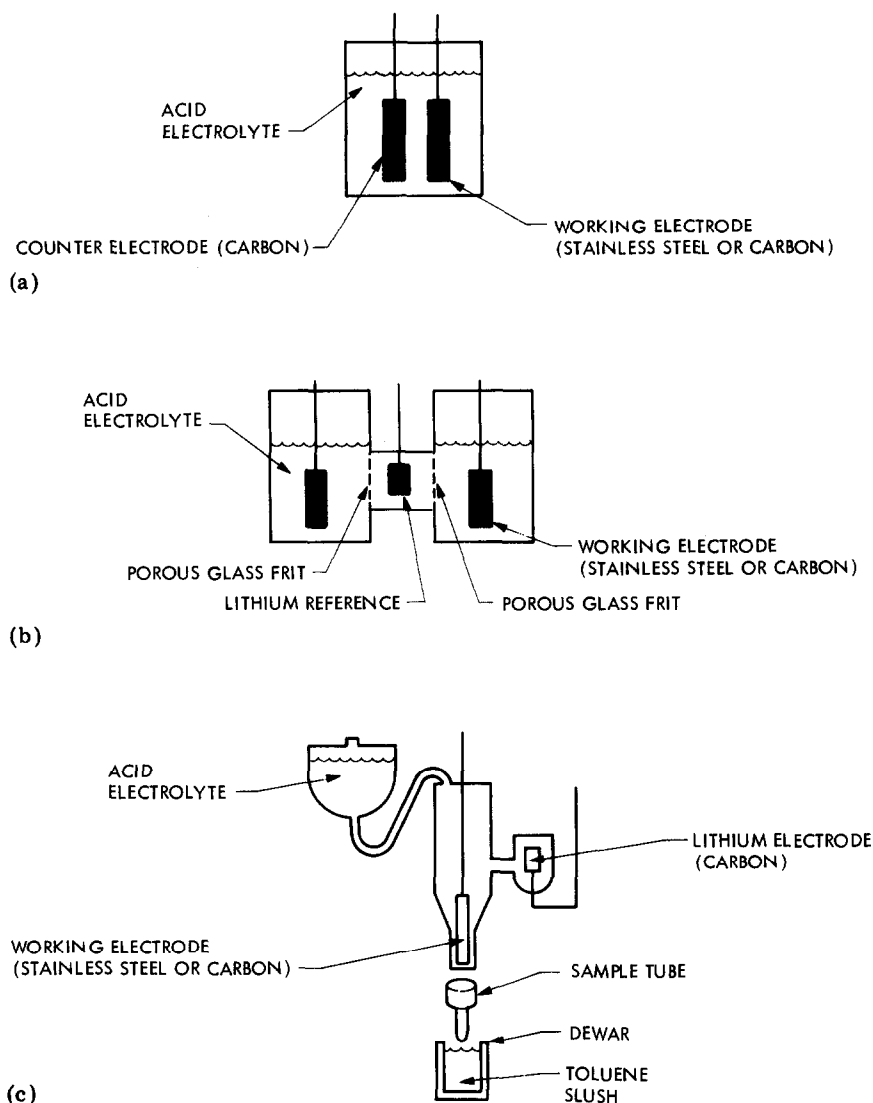
Fig. 1. Electrochemical cells. (a) Single compartment cell; (b) three compartment cell; (c) cell for ESR examination.

(iv) infrared spectroscopy (Digilab FTS-15C FTIR spectrometer, employing an aliquot cell with KBr windows and a nominal path length of 12 - 25 μm);

(v) Raman spectroscopy (Spex Model 14018 with a thermoelectrically cooled Hamamatsu R 955 photomultitube at a resolution of 2.5 cm^{-1}. An argon laser with a 70 mW power output served as a light source).

Results

Typical gas chromatographic analyses of samples from the anodic compartment of a three compartment cell are given in Fig. 2. Comparison of chromatograms of the fresh and oxidized samples indicates that the oxidation process results in the formation of the following species: Cl_2, SO_2, SCl_2, and S_2Cl_2. However, the Raman spectra differed in that they showed the presence of SO_2Cl_2 and the absence of SO_2. It would appear, therefore, that the SO_2 observed by gas chromatography may have resulted from disproportionation of SO_2Cl_2 during the analysis. Analysis of the spent electrolyte by atomic absorption spectrometry revealed the presence of small amounts of corrosion products of the stainless steel electrode, e.g., Fe^{3+} and Cr^{3+}. It is noted that these results are in agreement with those reported by Abraham and Mank [6].

Several runs were carried out in the ESR cell, Fig. 1(c), to identify radicals that may have been formed in the course of the oxidation process. In particular, attention was focussed on detection of the previously proposed hazardous compound ClO_2, which would be observed under the experimental conditions if it were present. In no case could this species be identified.
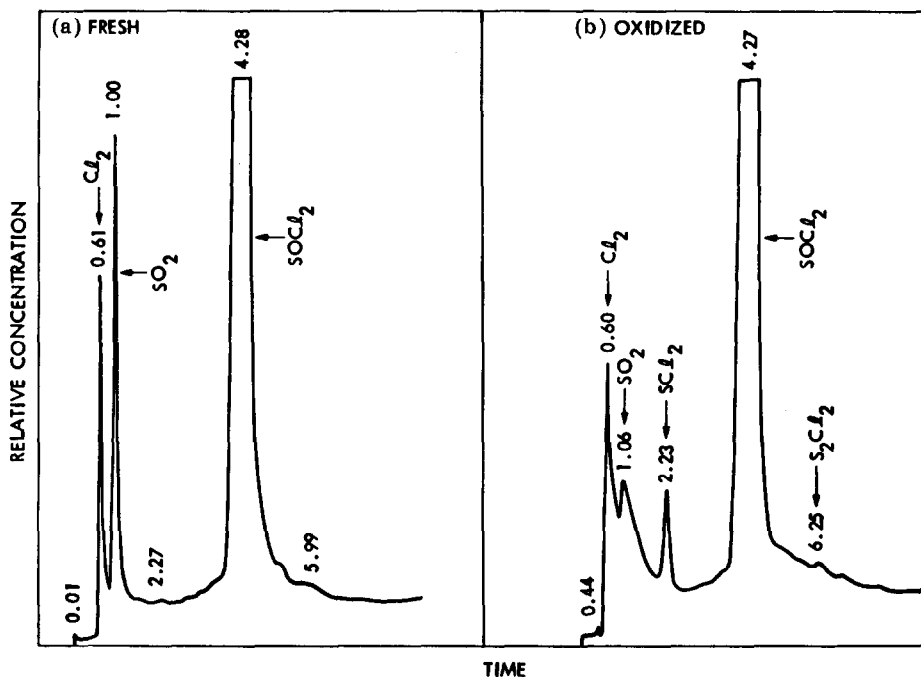

Fig. 2. Typical gas chromatograms for 1.9M $LiCl$/2.2M $AlCl_3$/$SOCl$ electrolyte: (a) fresh electrolyte; (b) oxidized electrolyte. The electrolyte was oxidized at 4.7 to 5.7 V (vs. Li/Li^+) at stainless steel, and the relative concentration scale is reduced 16 times from that used in (a).

Furthermore, the Raman spectra were also inconclusive with regard to the presence of another, potentially hazardous, compound, Cl_2O.

A question that naturally arises is whether these results are totally relevant, *i.e.*, whether the experimental cell simulates to a sufficient degree conditions prevailing within a real cell. Because of the large volume of the electrolyte employed and the reactivity of the oxidation products with the electrolyte, which may be concentration dependent, the reported results may not coincide with the composition in real cells. Furthermore, in real cells, oxidation products may diffuse to the cathode and react there, thus again altering the results.

To address this issue, samples were also prepared in a one compartment cell, Fig. 1(a), in which much less electrolyte was present, electrode spacing was less, and oxidation products could diffuse to the cathode and be reduced there. Samples were prepared by oxidation at stainless steel as well as at carbon surfaces, with a carbon counter-electrode in each cell. To account for the normal reduction products occurring at the carbon counter-electrode, samples were also prepared with a lithium anode.

Comparison of the amount of oxidation products formed in cells employing a Li electrode with those employing a carbon electrode shows a net loss in the concentration of Cl_2, SO_2 and S_2Cl_2, and an increase in the concentration of SCl_2. The decrease in Cl_2, SO_2 and S_2Cl_2 may be explained by electrochemical processes at the electrodes or, perhaps, the chemical reaction in the bulk of the solution. These results, together with those listed in Table 1, provide additional evidence that the products of $SOCl_2$ oxidation in batteries are: Cl_2, SO_2, SCl_2 and S_2Cl_2. Moreover, the concentration of these species may vary depending on local conditions inclusive of temperature, current density, and the degree of cell utilization.

TABLE 1

Summary of reaction products on oxidation of $LiCl–AlCl_3–SOCl_2$ electrolyte

| Method	Species identified	
	This work	Literature
Gas chromatography	SO_2*, Cl_2, SCl_2, S_2Cl_2	
Atomic absorption	Fe^{3+}, Ni^{2+}	
Electron spin resonance	Fe^{3+}, Cr^{3+}, S	
Infrared	SO_2Cl_2	Cl_2O, ClO_2 [3]
Raman spectroscopy	SO_2Cl_2	$AlCl_3 \cdot SOCl_2$ [10, 11], $2AlCl_3 \cdot SOCl_2$ [10, 11]
Cyclic voltammetry	—	Cl_2, SO_2Cl_2, SCl_2, S_2Cl_2 [6]

*SO_2 could be generated by thermal decomposition during introduction of sample to column.

Relevance to Li/SOCl$_2$ system

Results presented here were obtained under what may be designated as abnormal operating conditions, namely, intentional oxidation to simulate the cell charging process and forced overdischarge of anode and cathode limited cells, respectively. To illustrate, we contrast these operating modes against the normal discharge mode.

Normal mode

Figure 3 shows the functional elements of an Li/SOCl$_2$ cell during normal operation where the negative electrode serves as an electron source while the positive electrode acts as an electron sink. The corresponding overall electrochemical processes are, eqns. (1) and (2), respectively:

$$Li \longrightarrow Li^+ + e^- \tag{1}$$

$$SOCl_2 + 2e^- \longrightarrow \frac{1}{2} S + \frac{1}{2} SO_2 + 2Cl^- \tag{2}$$
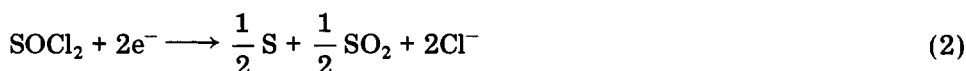
The cell voltage on discharge, $E(i)$, is positive as long as the cell delivers energy. The condition for the termination of the cell operation is $E(i) = 0$; in practice, however, the cell operation is terminated at an arbitrarily selected potential, $E(i) > 0$.

Figure 4(a) shows the potential distribution within a cell. The open circuit potential, $E(0)$, and the associated overpotentials $\eta_a(i)$ and $\eta_c(i)$ are
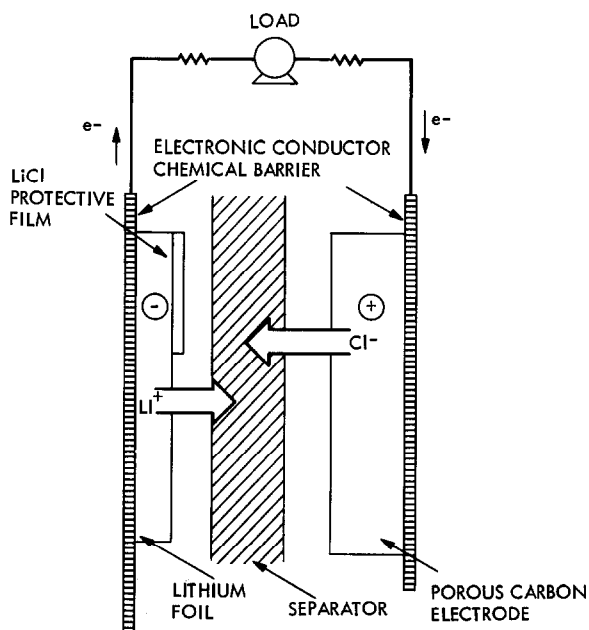

Fig. 3. Li/SOCl$_2$ cell — schematic.

CELL VOLTAGE

CELL OPEN CIRCUIT VOLTAGE

Li

η_a

η_c

C

0 1 2 3 4

E(i)

E(o)

CELL VOLTAGE

C

η_a

C

-1 0 1 2 3 4

E(o)

Li-ref

C

Li

Li dendrites

CELL VOLTAGE

Ni

Li

η_a

η_c

C

Li

1 2 3 4

Li-ref

C

Ni

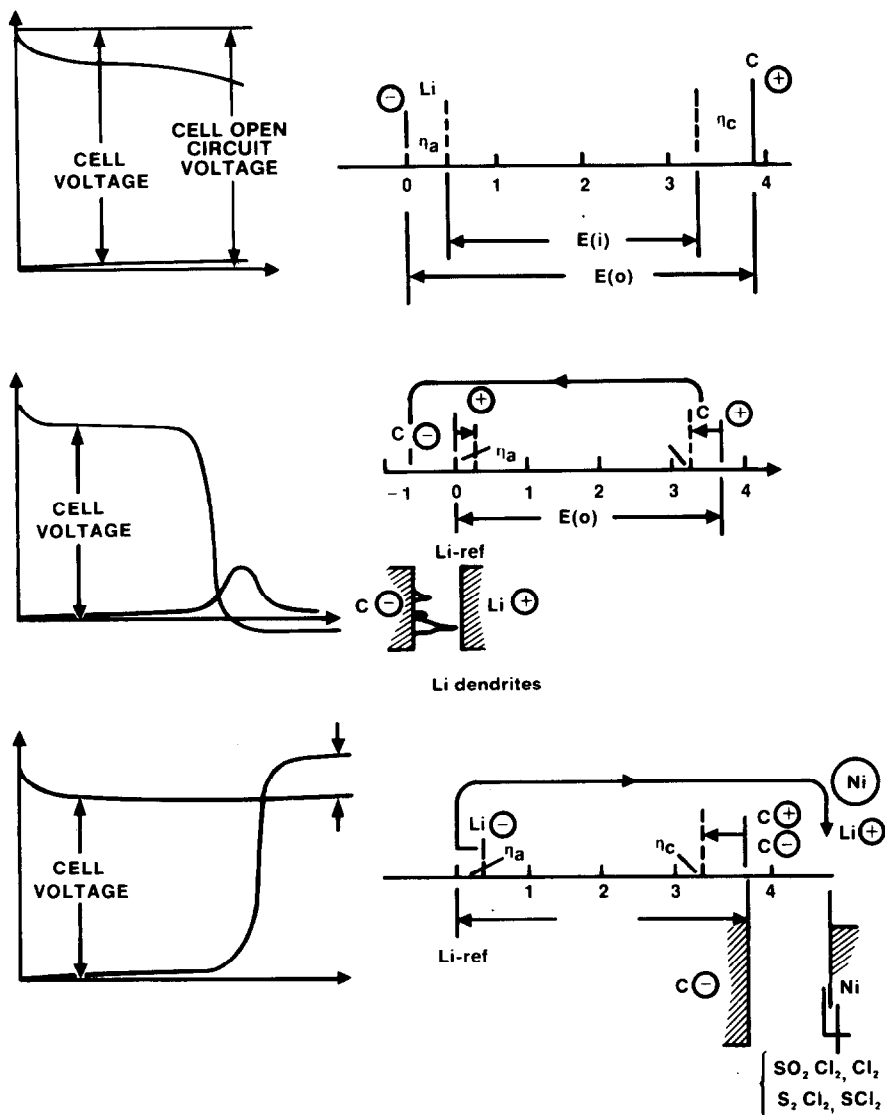$$\begin{cases} SO_2 Cl_2, Cl_2 \\ S_2 Cl_2, SCl_2 \end{cases}$$

Fig. 4. Representation of cell potential. (a) Normal discharge; (b) over discharge — cathode limited; (c) over discharge — anode limited.

indicated. For normal operation we have

$$E(i) = E(0) - [\eta_a(i) + \eta_c(i)] - R_c(i) \tag{3}$$

where R_c is the cell internal resistance.

If a single cell, or a group of in-series connected cells is defective, a new situation, that of reversal, i.e., $E(i) < 0$, may arise, particularly toward the end of the cell lifetime.

Forced overdischarge

Two of the most obvious cases, representing the behavior of cathode and anode limited cells on overdischarge, are illustrated in Fig. 4(b) and (c).

In the case of a cathode limited cell, the positive electrode ceases to operate (*e.g.*, due to plugging or inactivation of reactive sites) while sufficient electroactive material is still present to support the charge transfer reaction at the negative electrode. As shown in Fig. 4(b), the cathode potential, measured *vs.* the Li/Li$^+$ reference electrode, becomes less positive and, upon continuing overdischarge, the electrode is forced to a potential negative to the Li electrode, *i.e.*, the affected cell shows the negative cell voltage, $E(i) < 0$. Under these conditions, the electrochemical reactions at the carbon electrode are different, even though the Li electrode still functions as an electron source. At the carbon electrode the dominant reaction is eqn. (4)

$$Li^+ + e^- \longrightarrow Li \qquad (4)$$

The net result is the electrodeposition of metallic Li on the carbon matrix. In regard to safety, this situation is not resolved. For example, the electrodeposition of metallic Li may provide an electronic path and render the cell operation safe [7]. On the other hand, a mixture of Li, carbon, and sulfur in the presence of SOCl$_2$ has been found to be explosive [8].

The opposite occurs in the anode limited cells, where the Li metal is either used up before the plugging of the porous structure of the positive electrode, or otherwise made electrochemically inactive (*e.g.*, because of poor connection to the bipolar plate). As the current is forced across the defective cell, the potential of the negative electrode becomes more positive, finally exceeding the potential of the carbon electrode, Fig. 4(c). Here again, the affected cells suffer the cell voltage reversal. The carbon electrode acts as an electron sink, but the anodic reaction is completely different, *i.e.*, the electron source is either due to the oxidation of the bipolar plate or due to the oxidation of the components of the electrolyte phase, *e.g.*, AlCl$_4^-$ and SOCl$_2$.

Intercell currents

The conditions of current/potential reversal are not restricted to the presence of defective cells in a battery. Electrochemical reactions responsible for the initiation of intercell currents are inherent even in a properly constructed battery of a reserve type because of the manifold system that is used to transport the electrolyte from the storage reservoir to the individual cells. While serving this function, the manifold also provides a common electrolyte path between the in-series connected cells. This path permits parasitic intercell current to flow. The magnitude of this current is a function of several factors [9]. When the intercell currents exceed a critical value, a partial reversal of current takes place in the end cells, or in the cells adjacent to the defective one. This reversal of current results in the electroreduction deposition of metallic Li at the negative plates in cells located at the negative end of a battery, and in the electro-oxidation of an electrolyte
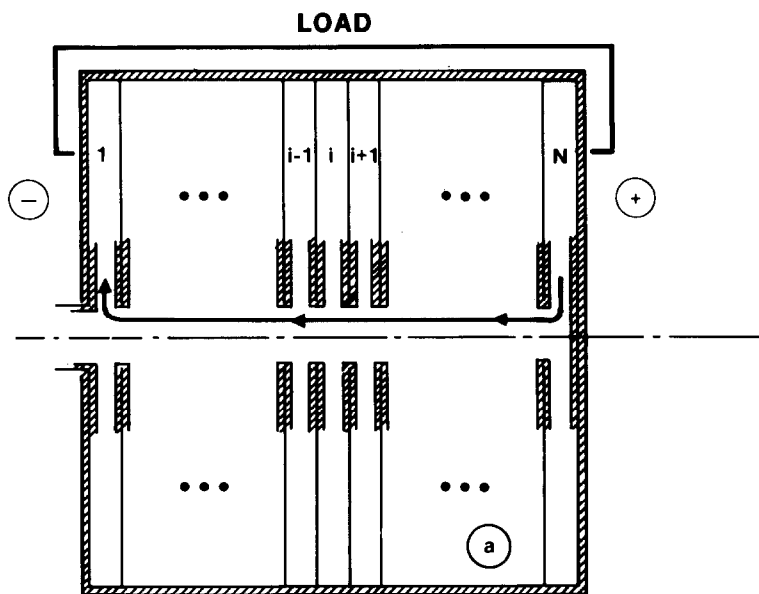
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Fig. 5. Reserve type, bipolar Li/SOCl₂ battery. Intercell current indicated by arrows.

at the positive plates located at the positive end of a battery. The action of intercell current at the negative end of a battery is equivalent to a forced overdischarge of cathode limited cells, while at the positive end, it represents the conditions associated with a forced overdischarge of anode limited cells.

Conclusions

The scope of the present investigation was limited to the examination of safety aspects arising from abnormal cell operation and being of a chemical nature. Thus, purely uncontrolled events due to internal shorts, either initially present or arising from partial or total cell current reversal, are not included. Also not included is a discussion of conditions associated with the forced overdischarge of cathode limited cells, i.e., where Li is deposited onto or within the porous structure of the carbon electrode, especially in the presence of an excess of $SOCl_2$ [8].

A major concern with the results reported here and their relevance to the $Li/SOCl_2$ batteries, especially those designed for high discharge rate applications, is the large excess of electrolyte and current densities in experimental cells. This large excess of electrolyte was employed here because the objective was to identify the primary products of electrolytic oxidation and not the secondary products that can be formed from them by inter-reaction (in the three compartment cell) or with the cathodic reaction products (in the one component cell). These latter reactions may be dependent on con-

centration, current density, and also cell design. Undoubtedly, these (subsequent) reactions do occur in actual cells and may result in other products not identified herein.

At present there is no evidence that the conditions of current or potential reversal and subsequent oxidation of the $LiCl-AlCl_3-SOCl_2$ electrolyte produce hazardous species in sufficient quantities to initiate explosive behavior. This conclusion applies to conditions investigated, *i.e.*, cell voltage between 4.7 and 13 V, current densities of 0.5 - 10 mA/cm^2 and a temperature range between 25 and 35 °C.

Acknowledgements

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