

Chemical and electrochemical processes in some lithium–liquid cathode batteries*

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Abstract

Some important chemical and electrochemical processes in the Li/SO₂, Li/SOCl₂ and Li/SO₂Cl₂ batteries, and the halogen and interhalogen modifications of the latter two systems, are reviewed. While the emphasis is on the data obtained in the author's laboratory during the past ten years, relevant results of others are included to put our work in the context of the diverse efforts on Li–liquid cathode batteries.

Introduction

Lithium–liquid cathode batteries comprise a versatile group of high-energy-density power sources with a variety of military and civilian applications. Prominent members of this class of batteries are listed in Table 1. They include the traditional primary batteries Li/SO₂, Li/SOCl₂ and Li/SO₂Cl₂, and their modifications Li/'SOCl₂ + BrCl', Li/SO₂Cl₂ + Cl₂ and Li/'SOCl₂ + SO₂Cl₂' [1–4]. Lately, the development of an Li/SO₂ secondary battery has been actively pursued [5]. Another class of Li–liquid cathode cells which has received recent attention utilizes halo-carbons such as tetrachloroethane as cathodes [6]. The Li/BrF₃ cell [7], exhibiting an OCV of 5.1 V, has the highest theoretical specific energy and volumetric energy density among the various systems listed in Table 1; however, its development has not yet advanced beyond the laboratory test cell stage. The Li–sulfur rechargeable system may be characterized as an Li–liquid cathode cell of the 'second kind' since the liquid cathode in this case is a solution of lithium polysulfides, Li₂S_n, $n = \sim 8$, in tetrahydrofuran (THF) [8]. The poor rechargeability of this cell, owing to a self-discharge mechanism mediated by reactions of soluble sulfide discharge products, is an example of problems that can arise in the development of secondary Li–liquid cathode batteries in which the discharge products are soluble in the electrolyte. The self-discharge rate may be reduced by making the products less soluble. The primary Li/Li₂S_n battery utilizing a THF–toluene/LiClO₄ electrolyte is based on this concept [9].

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TABLE 1
 Characteristics of some lithium-liquid cathode batteries

System	Cell discharge reaction	Open circuit voltage (OCV) (V, at room temperature)	Theoretical specific energy (W h kg ⁻¹)	Theoretical volumetric energy density (W h l ⁻¹)
Li + BrF ₃	3Li + BrF ₃ → 3LiF + 1/2Br ₂	5.10	2600	4650
Li/SO ₂ Cl ₂	2Li + SO ₂ Cl ₂ → 2LiCl + SO ₂	3.90	1400	1950
Li/SO ₂ Cl ₂ + Cl ₂ ¹¹	2Li + Cl ₂ → 2LiCl	3.90	1420	2000 ^a
	2Li + SO ₂ Cl ₂ → 2LiCl + SO ₂			
Li/1:1SO ₂ Cl ₂ :SOCl ₂	2Li + SO ₂ Cl ₂ → 2LiCl + SO ₂	3.90	1436	1975
	4Li + 2SOCl ₂ → 4LiCl + S + SO ₂			
Li/SOCl ₂ + BrCl ¹¹	Cl ₂ + 2Li → 2LiCl	3.90	1563	2180 ^a
	BrCl + 2Li → LiBr + LiCl			
	Br ₂ + 2Li → 2LiBr			
	4Li + 2SOCl ₂ → 4LiCl + S + SO ₂			
Li/SOCl ₂	4Li + 2SOCl ₂ → 4LiCl + S + SO ₂	3.65	1471	2000
Li/Cl ₂ CHCHCl ₂	2Li + Cl ₂ CHCHCl ₂ → 2LiCl + ClCH = CHCl	3.21	945	1310
Li/LiAlCl ₄ · 3SO ₂ (secondary)	3Li + LiAlCl ₄ · 3SO ₂ → LiAlCl(3SO ₂) + 3LiCl	3.20	660	940 ^a
Li/SO ₂ (primary)	2Li + 2SO ₂ → Li ₂ S ₂ O ₄	2.90	1098	1353
Li/THF, Li ₂ S ₈	14Li + Li ₈ S ₈ → 8Li ₂ S	2.40	2446	2855 ^a

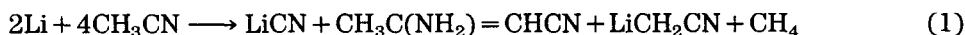
^aDue to lack of reliable density data these values are estimated.

It is to be noted that this paper is not intended as a comprehensive review of Li-liquid cathode batteries. Rather, its purpose is to present a summary of the work carried out in the author's laboratory during the past ten years and to put our work in the context of the diverse efforts on Li-liquid cathode batteries.

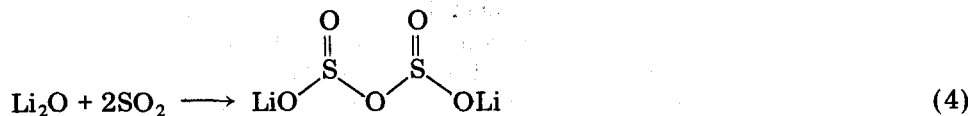
Lithium-sulfur dioxide batteries

The stability of lithium-liquid cathode batteries is intimately connected with the formation of an insoluble, passivating film on the Li anode surface when the Li comes in direct contact with the liquid cathode. These films are described as solid-electrolyte-interphases, or SEI [10], since they are impermeable to electrolytes and other liquid reactants while transporting Li^+ across them.

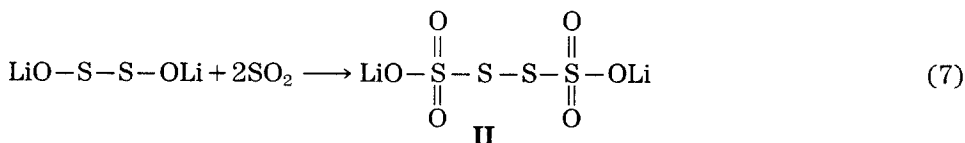
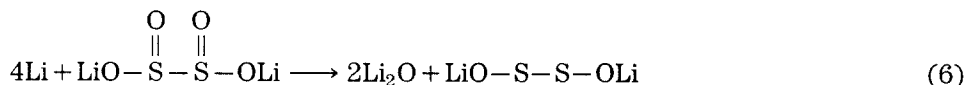
The need for a passivating film on the Li anode in order to obtain a stable liquid cathode cell can be illustrated with the $\text{Li}/\text{CH}_3\text{CN}$, LiBr/SO_2 primary cell. Lithium reacts spontaneously with CH_3CN to produce a number of products including CH_4 [11], eqn. (1).



This reaction does not occur in the presence of SO_2 , however, and the Li/SO_2 primary cell is extremely stable in the temperature range -40 to 70 °C. Evidently, the Li anode becomes passivated by its reaction products with SO_2 . The conventional wisdom has been that this passivating film is $\text{Li}_2\text{S}_2\text{O}_4$, a conclusion apparently arrived at from analogy with the cell discharge product, which is $\text{Li}_2\text{S}_2\text{O}_4$. Our studies [12, 13] have shown that the film is heterogeneous in nature being composed of Li_2S , Li_2SO_3 , $\text{Li}_2\text{S}_2\text{O}_5$, $\text{Li}_2\text{S}_n\text{O}_6$ with $n \geq 3$, and $\text{Li}_2\text{S}_2\text{O}_4$ [12, 13]. We have also identified an increased growth rate for this Li surface film during storage of partially discharged cells [12], and during cell discharge [13]. Our proposed mechanism for formation of the various components of the film is presented in eqns. (2)–(8).



The formation of $\text{Li}_2\text{S}_n\text{O}_6$ may occur through the following sequences of reactions starting with $\text{Li}_2\text{S}_2\text{O}_4$

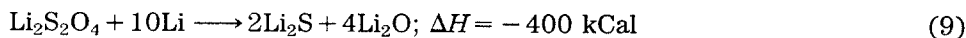


Our results have been confirmed by Bittner [14] and Anderson [15]. Bittner has presented a bilayer model for the Li passivation layer: a primary layer which protects the anode as well as being the cause of some of the voltage delay, and a secondary layer which induces a polarization that inhibits high-rate discharge. Bittner also found the growth rate of the passivating film to be higher during storage of partially discharged cells and he has attributed it to defects in the primary layer arising from the partial discharge. The defects may be grain boundaries, lattice defects, or cathode impurities which cause an overall increased electronic conductivity for the primary passivation layer.

The composition of the electrolyte appears to affect the nature of the Li passivating film since, in the all-inorganic secondary Li/SO₂ cell containing the $\text{LiAlCl}_4 \cdot x\text{SO}_2$ electrolyte, it is apparently LiCl [5].

The principal discharge product in the Li/SO₂ primary cell is $\text{Li}_2\text{S}_2\text{O}_4$, and it appears that ours was the first quantitative determination of it from commercial cells [11]. $\text{Li}_2\text{S}_2\text{O}_5$ and $\text{Li}_2\text{S}_n\text{O}_6$ have been identified as minor discharge products at high rates and/or elevated temperatures [16, 17]. According to Dey and co-workers [5], the discharge products in the secondary Li/SO₂ cell are LiCl and a complex formed between an Li-aluminum sulfuroxy compound and carbon. Mammone and Binder have presented qualitative evidence for dithionite in this cell although they did not establish that it was $\text{Li}_2\text{S}_2\text{O}_4$ [18]. In view of these results and the fact that the open-circuit potential of the all-inorganic Li/SO₂ cell is 3.2 V, it is tempting to propose that the discharge products in the secondary cell are LiCl, and an Li-aluminum-dithionite having the possible formula $\text{LiAlCl}(\text{S}_2\text{O}_4)$ or $\text{LiAl}(\text{S}_2\text{O}_4)_2$. Certainly, substantial further work remains to be done for the full elucidation of the discharge chemistry of the Li/SO₂ secondary cell.

Our studies of the phenomenology of the safety hazards in Li/SO₂ primary cells, coupled with considerations of the energetics of the reactions involving various cell components, including products identified, have pointed out reactions (9) and (10) as being most relevant to the forced overdischarge-related safety hazards of the cells [16].





The values of x and y in eqn. (10) are presently unknown and the possibility of other decomposition products cannot be ruled out. These reactions may be relevant to the safety of the secondary Li/SO₂ cell also.

Safety concerns, including the fact that the cell utilizes SO₂ under pressure, have precluded widespread consumer acceptance of Li/SO₂ primary cells. However, they have played a prominent role as military batteries. Figures 1 and 2 present discharges of commercial Li/SO₂ cells at several current and temperature conditions. Typical Li/SO₂ D-cells have a specific energy of about 250 W h kg⁻¹ and a volumetric energy density of approximately 400 W h l⁻¹ at a power drain of 5 W.

Lithium-sulfur oxychloride batteries

As indicated in Table 1, the Li-sulfur oxychloride cells are some of the very high energy density Li power sources available today. The data presented in Table 2 for D-size cells show that they are capable of more than twice the energy density of Li/SO₂ cells.

Li/SOCl₂ cells

Figure 3 presents the cell voltage, individual electrode potentials, internal and external temperatures, and pressure data we have obtained for a specially instrumented, cathode-limited, C-size Li/SOCl₂ cell [19]. The discharge was

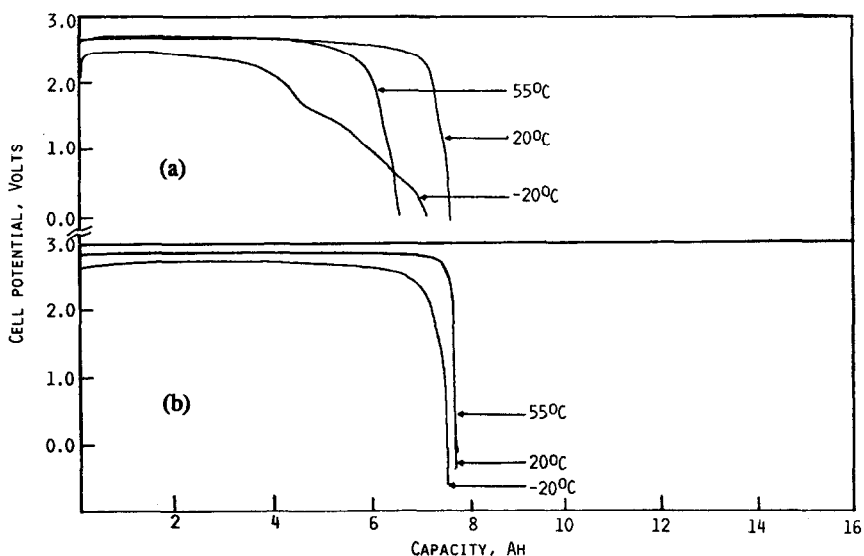


Fig. 1. Discharge of Li/SO₂ D-cells at different temperatures. (a) Discharge at 2.0 A; (b) discharge at 0.2 A.

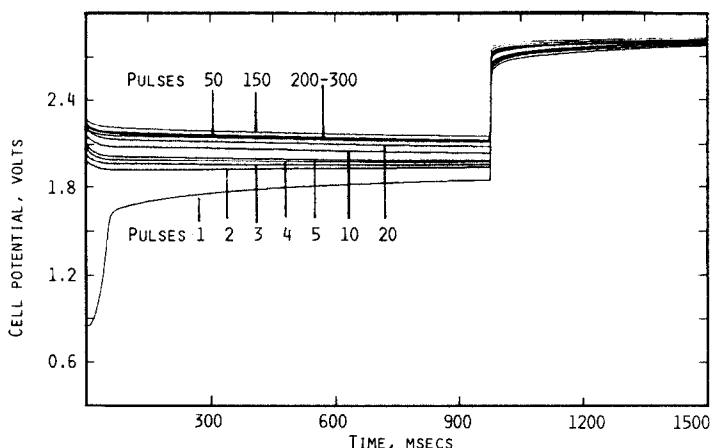


Fig. 2. 25 A ($\sim 50 \text{ mA cm}^{-2}$) pulse discharge of Li/SO₂ cells. Pulse width = 1 s. Each pulse is followed by a 9 s rest period.

TABLE 2

Energy densities^a of Li/SO₂ and Li/sulfur oxychloride D-cells

Cell	Voltage (V)	Capacity (A h)	W h l ⁻¹	W h kg ⁻¹
Li/SO ₂	2.7	7	400	250
Li/SOCl ₂	3.5	12	820	450
Li/SO ₂ Cl ₂	3.7	14	1000	550

^aFor discharge at low to moderate rates, actual values may vary from one manufacturer to another and depending on design considerations.

carried out at a constant current of 2 A, equivalent to $\sim 10 \text{ mA cm}^{-2}$, at room temperature. Similar data for discharges at other temperatures and currents are presented in ref. 19. The internal temperature of the cell in Fig. 3 rose to $\sim 50 \text{ }^\circ\text{C}$ and remained at that value almost until the end of normal discharge. During this time the pressure attained a maximum value of only 25 psig. The highest internal temperatures and pressures were attained during the early stages of cell voltage reversal and reached values of $\sim 115 \text{ }^\circ\text{C}$ and $\sim 140 \text{ psig}$, respectively. The values of pressure, calculated at points A and B, on the basis of the discharge reaction in Table 1 are given in Table 3.

The pressures attained in the cell are significantly lower than that expected on the basis of the amount of SO₂ produced in the cell. A chemical process responsible for such low pressures may involve the complexation of SO₂ by LiAlCl₄ to lower its vapor pressure significantly. Based on the work of Dhamelincourt *et al.* [20], we can write the equilibria in Scheme I to describe the related cell chemistry. The vapor pressure of Li(SO₂)₃AlCl₄ is less than one atmosphere at room temperature.

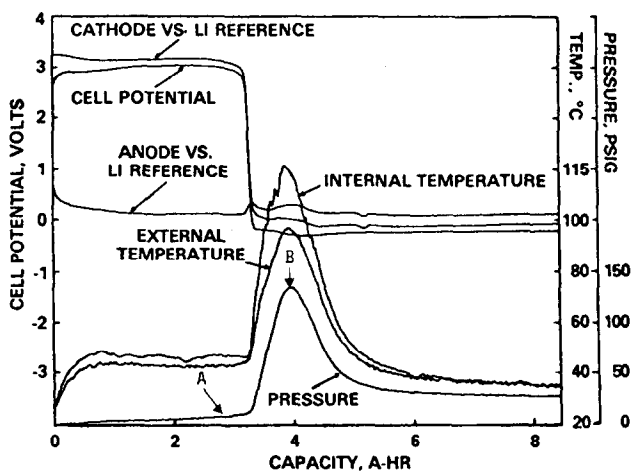


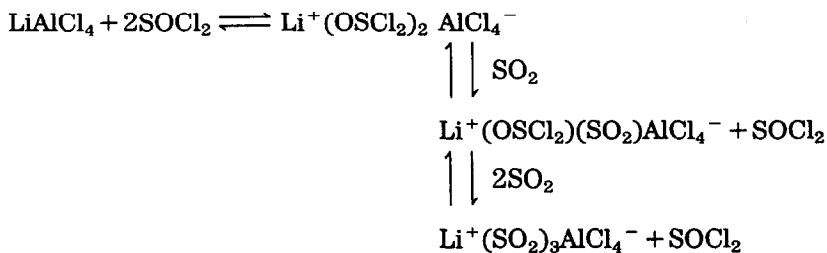
Fig. 3. Temperature, pressure, and voltage data for an uncatalyzed, cathode-limited Li/SOCl_2 C-size cell discharged at 2.0 A at room temperature.

TABLE 3

Observed and calculated pressures^a at points A and B in the C-size Li/SOCl_2 cell shown in Fig. 3

		A	B
Temperature (°C)		50	115
Pressure (psig)	Found	~20	~140
	Calcd.	130	≥ 500

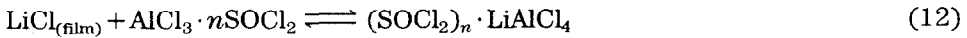
^aThe basis of the calculation is discussed in ref. 19.



Scheme 1.

It should be noted here that absorption of SO_2 into carbon might be an additional reason for the observed lower pressure [21]. Scheme 1 implies that from the point of view of safety of Li/SOCl_2 cells, a high concentration of LiAlCl_4 is favored. Besides, a high concentration of LiAlCl_4 is required in high rate Li/SOCl_2 cells to overcome Li^+ concentration polarization effects. However, high concentrations of LiAlCl_4 may exacerbate Li corrosion and

increase voltage delay owing to enhanced corrosion of the Li anode via exchange reactions between the LiCl passivating film and the electrolyte, as shown in eqns. (11) and (12).



The proposed use of low concentrations of LiAlCl_4 [22] or alternative salts such as LiGaCl_4 [23] to alleviate voltage delay is in accordance with the mechanism of Li corrosion illustrated in reactions (11) and (12).

The voltage, temperature, and pressure data for an Li-limited, C-size Li/SOCl₂ cell, corresponding to a discharge current of 2 A at room temperature, are depicted in Fig. 4. Appreciably lower internal temperatures and pressures than those measured in the cathode-limited cell are produced in this cell. It is clear from a comparison of Figs. 3 and 4 that cathode polarization (and reactions associated with it) is the principal source of heat during discharge and overdischarge of Li/SOCl₂ cells.

A number of chemical and electrochemical reactions occur during forced overdischarge of Li-limited Li/SOCl₂ cells [24]. As can be seen in Fig. 4 the cell maintains a relatively steady anode potential owing to the regenerative processes shown in eqns. (13)–(17).

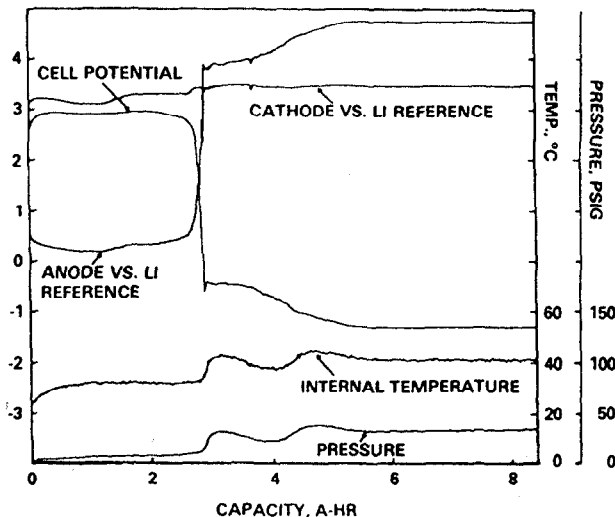
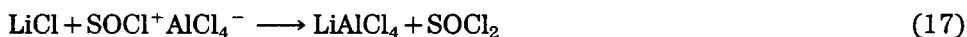
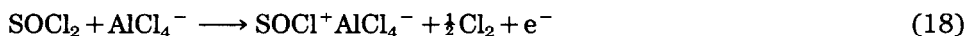


Fig. 4. Temperature, pressure, and voltage data for an uncatalyzed, Li-limited Li/SOCl₂ C-size cell discharged at 2.0 A at room temperature.



In addition, oxidation of SOCl_2 to produce SO_2Cl_2 , $\text{SOCl}^+ \text{AlCl}_4^-$, Cl_2 , and SCl_2 or its complex with AlCl_3 may also occur at the anode [24].



Further discussion of cell phenomenology during overdischarge will be presented later in this paper. We have also shown that processes paralleling those in the overdischarge of anode-limited cells occur during 'charging' of Li/SOCl_2 cells [24, 25]. A cell may be 'charged' for an extended period of time at low-to-moderate rates with little net gain in products. Such a cell can be subsequently discharged to yield the same capacity as that prior to the charge [24, 25]. The above described cell chemistry and behavior first identified by us have been confirmed by others [26, 27]. It is interesting to note here that these oxidation/reduction reactions of LiAlCl_4 also form the basis of overcharge protection of the secondary Li/SO_2 cells [5].

Lower cathode polarization and higher capacity have been achieved in Li/SOCl_2 cells by the use of certain additives to the cathodes, collectively termed 'catalysts'. The data in Fig. 5, given for a cell identical to the one in Fig. 3 except for the fact that its cathode contains a cobalt tetraazaannulene (CoTAA)-based catalyst, illustrate this. In addition to increases in load voltage and capacity, the temperature and pressure are also lowered by the addition of the catalyst to the cathode. Data presently available indicate that various levels of improvement of the Li/SOCl_2 cell can be brought about by the use of a number of different cathode additives including Cu [28], CuCl_2 [29], Pt [30], CoO [31], iron phthalocyanine (FePc) [32], monomeric and polymeric

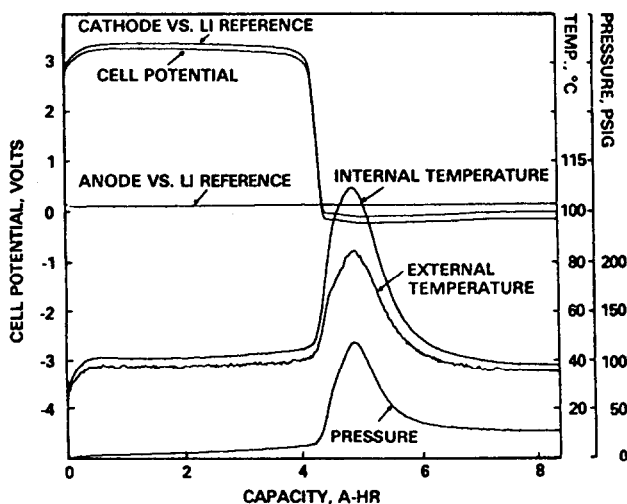


Fig. 5. Temperature, pressure, and voltage data for a Co-TAA catalyzed, cathode-limited Li/SOCl_2 C-size cell discharged at 2.0 A at room temperature.

cobalt phthalocyanine (CoPc) [32], Fe and Co tetraphenylporphyrin [32] and cobalt dibenzotetraazaannulene (CoTAA) [33, 34, 19]. The metallomacrocylic porphyrins, phthalocyanines and tetraazaannulenes have been the most widely studied catalysts.

The metallomacrocycles may be more accurately designated as 'catalyst precursors' because our recent analytical results [35] indicated that they undergo substantial chemical changes including decomposition during activation of the carbon–metallomacrocycle mix by heat treatment in the 600–800 °C range. The 'actual catalyst' is a product of this heat treatment. We have also found that a number of previously unidentified transition metal phthalocyanines, such as CuPc, NiPc, MnPc and VOPc, are also desirable catalyst precursors for the Li/SOCl₂ cell [36].

In our recent studies to unravel the mechanism of electrocatalytic reduction of SOCl₂ by metallomacrocycles we have made the following experimental observations.

- The precursor from which the catalyst is incorporated into the carbon affects its activity. For example, nitrate, carbonate, and carbonyls of cobalt were inactive, while cobalt phthalocyanine, and cobalt tetraazaannulene resulted in active catalysts [36, 19].

- Transition metal phthalocyanines were more active than those containing main group metals. This is exemplified by the data in Table 4 [35, 36].

- Carbon/transition metal phthalocyanine mixtures heat treated at ≥ 600 °C resulted in cathodes with increased capacity and/or voltages, compared with uncatalyzed electrodes, although UV–visible, IR spectral and X-ray diffraction studies indicate substantial decomposition of the macrocyclic complexes at these temperatures [35].

TABLE 4

Capacities of Li/SOCl₂ cells containing carbon electrodes sintered at 600 °C with metal phthalocyanines

Current = 10 mA cm⁻², temperature = 20 °C

Catalyst (5 wt.%)	Mid-discharge voltage (V)	Average carbon utilization (A h g ⁻¹)
Uncatalyzed	2.93	1.35
Pc	2.92	1.57
LiPc	3.19	1.62
SiPcCl ₂	3.10	1.70
MgPc	3.15	1.76
CoPc	3.15	1.90
VOPc	3.34	1.98
MnPc	3.29	2.21
NiPc	3.12	2.17
CuPc	3.16	2.26
ZnPc	3.08	1.60

Any mechanism put forward to explain the catalytic reduction of SOCl_2 on porous carbon cathodes must reconcile the fact that both the load voltage and discharge capacity are increased by the metallomacrocylic additives. An increase in capacity in a 'truly catalyzed' reduction requires that the discharge stoichiometry be altered by the catalyst. This was probably the basis for proposing $\text{Li}_2\text{S}_2\text{O}_4$ and $\text{Li}_2\text{S}_2\text{O}_3$ as possible discharge products in metallomacrocycle-catalyzed Li/SOCl_2 cells [32–34]. Subsequent analytical work proved this not to be the case. We have found that the principal discharge products in both CoTAA- and metal-phthalocyanine catalyzed cells are LiCl , S , and SO_2 , and that the amount of LiCl agreed with the established discharge reaction shown in Table 1. How does, then, one account for the higher capacity in catalyzed cells? The catalyst may play a dual role. First, it may lower the activation energy for electron transfer from the carbon substrate to SOCl_2 . This would account for the higher voltage. Second, the catalyzed carbon may have a larger adsorption capacity for SOCl_2 , thereby increasing the concentration of SOCl_2 being reduced on the cathode. It is possible that carbon/metallomacrocycle mixtures, when heat treated at $\geq 600^\circ\text{C}$, undergo structural changes, specifically in the carbon, which are favorable for enhanced adsorption of SOCl_2 . The catalyst may also change the LiCl morphology. This can accommodate more LiCl in the cathode; hence, more cell capacity.

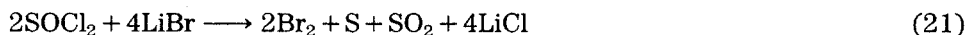
Improvements in the performance and safety of the Li/SOCl_2 cell have been sought by the use of interhalogen compounds as additives. Feiman *et al.* [37] studied the effect of ICl_3 and ICl and reported improvements in the voltage delay characteristics of the battery. Liang *et al.* [38], Krehl and Liang [39], and Murphy *et al.* [40] reported that the addition of BrCl to the Li/SOCl_2 cell resulted in a higher open-circuit potential, increased cell capacity, better low temperature performance, and improved safety features. Li/SOCl_2 cells containing BrCl are commonly referred to as BCX cells.

We have determined [41] that, in SOCl_2 and $\text{SOCl}_2/\text{LiAlCl}_4$, BrCl is dissociated as $2\text{BrCl} \rightleftharpoons \text{Br}_2 + \text{Cl}_2$ with a degree of dissociation, α , of about 0.45. The equilibrium constant, K_{eq} , calculated from eqn. (20) was about 0.17. The values of K_{eq} and α are of the same magnitudes as found in CCl_4 . This information, coupled with spectroscopic and electrochemical data, suggests only weak interactions between SOCl_2 and BrCl [41]. Similarly, based on spectroscopic data, we concluded that only weak interactions exist between SOCl_2 and Cl_2 , Br_2 or I_2 [41].

$$K_{\text{eq}} = \frac{\alpha^2}{4(1-\alpha)^2} \quad (20)$$

We have determined that the discharge chemistry of the Li/SOCl_2 cell is significantly modified by the addition of BrCl to the electrolyte [42]. Our analytical data were interpreted in terms of the principal discharge reactions shown in Table 1. However, there was evidence for regeneration of Br_2 from a chemical reaction between LiBr and SOCl_2 (eqn. (21)), and for the formation

of S_2Br_2 , SO_2Br_2 , SO_2Cl_2 , $SOCl_2$, S_2Cl_2 and S_2Br_2 [42] from reactions involving Br_2 and $BrCl$.



Our studies of D-size $Li/SOCl_2 + BrCl$ cells have led to the conclusion that partial discharge of these cells to certain depths, followed by storage at ambient temperature, deleteriously affects their performance [42]. Figure 6 presents typical data we have obtained. In this investigation, several BCX D-cells, with typical rated capacities of ~ 13 A h at 0.20 A, were first discharged to a depth of 3 A h. These cells were then stored for one year at ambient temperature, and then discharged at 0.20 A at the same temperature. The cells showed severe voltage depression. Although a capacity of ~ 10 A h was obtained, the average load voltage was ~ 1.25 V. Fresh BCX cells stored under identical conditions for one year showed a self-discharge of ~ 1 A h. However, their post-storage discharge voltage, at 0.20 A, was identical to that found in fresh cells. Another series of BCX cells was initially discharged by 0.7 A h. Storage at room temperature for one year, followed by discharge at 0.20 A, showed only a small loss in capacity and the cell voltages were similar to that of undischarged cells stored for the same length of time. It appears that discharge of BCX cells into the $SOCl_2$ reduction region and subsequent storage is deleterious. Sulfur halides, sulfuryl halides, and Br_2 formed in these partially discharged cells may react with the Li anode causing excessive anode passivation, and consequent voltage delay and voltage depression. Under identical test conditions, conventional $Li/SOCl_2$ D-cells of identical design as the BCX D-cells, either fresh or partially discharged, showed practically no self-discharge or deterioration in performance as a result of extended storage at room temperature. More recent results from Wilson Greatbatch, Inc., suggests possible solutions to some of the storage-related problems of the BCX cells [43].

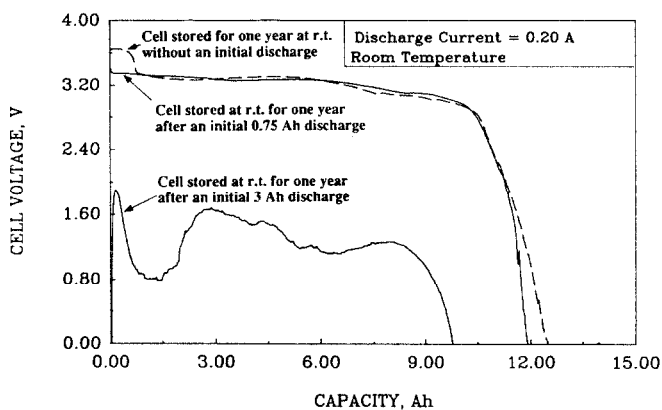


Fig. 6. Effect of partial discharge and storage at room temperature on the subsequent discharge behavior of $Li/SOCl_2$ cells containing $BrCl$.

Li/SO₂Cl₂ cells

We have investigated the chemistry and electrochemistry of Li/SO₂Cl₂ and Li/"SO₂Cl₂ + Cl₂" cells, designated in this paper as SC and CSC cells, respectively [44]. LiCl from discharged SC and CSC cells was quantitatively determined, and it agreed well with the discharge reactions given in Table 1. Both CSC and SC D-cells exhibited practically identical discharge performance; neither the voltage profiles nor the capacities of the two types of cells exhibited significant differences. It is known that SO₂Cl₂ dissociates as SO₂Cl₂ ⇌ Cl₂ + SO₂. The dissociation constant of this equilibrium has been determined to be 0.01 [45], which translates into an equilibrium Cl₂ concentration of ~0.35 M. When Cl₂ is bubbled into an LiAlCl₄/SO₂Cl₂ solution, the above dissociation equilibrium is shifted to the left [44, 45]. It may be estimated that in the CSC cell electrolyte containing 0.45 M Cl₂ in 1 M LiAlCl₄/SO₂Cl₂, substantially undissociated SO₂Cl₂, and free Cl₂ of ~0.5 M are present. Thus, the Cl₂ concentration in SC and CSC cell electrolytes turns out to be almost the same, and this probably explains why both SC and CSC cells exhibit nearly the same upper plateau capacity. The low-temperature (e.g., -20 °C) performance of Li/SO₂Cl₂ cells is inferior to that of Li/SOCl₂ cells. We have found that the low-temperature capacities of CSC and SC cells are influenced by the discharge rate, with better capacities being obtained at higher rates [44]. This unusual behavior is believed to be a consequence of the physical and transport properties of Li⁺-solvent complexes formed during the course of the discharge [20].

We have found that improved low temperature capacity can be obtained in the cells utilizing a mixed solvent electrolyte comprised of LiAlCl₄ dissolved in SOCl₂ and SO₂Cl₂ [46]. Results we obtained from laboratory test cells are depicted in Fig. 7. Encouraged by these results we constructed and tested C-size cells containing SOCl₂:SO₂Cl₂/LiAlCl₄ mixed electrolytes [47]. The performance of these cells, in terms of voltage delay characteristics, capacity, low-temperature rate capability, and storage at 70 °C, was superior to that of conventional Li/SOCl₂ cells.

More recently, we have studied mixed inorganic electrolytes based on LiAlCl₄ solutions in SO₂Cl₂/SO₂ and SO₂Cl₂/SOCl₂/SO₂. Results obtained in laboratory test cells appear to show that they are superior to the conventional SO₂Cl₂-LiAlCl₄ electrolytes. Representative data are presented in Figs. 8 and 9.

Overdischarge behavior of Li-sulfur oxychloride cells

During the more than ten years of our involvement with Li-sulfur oxychloride cells, we have had the opportunity to examine the overdischarge behavior of a variety of these cells. We have found that the overdischarge behavior, including potential profiles, internal temperature, and pressure, of all of them largely depends on the configuration of the cell, i.e., the ratio of the initial Li to cathode capacity, rather than on the nature of the

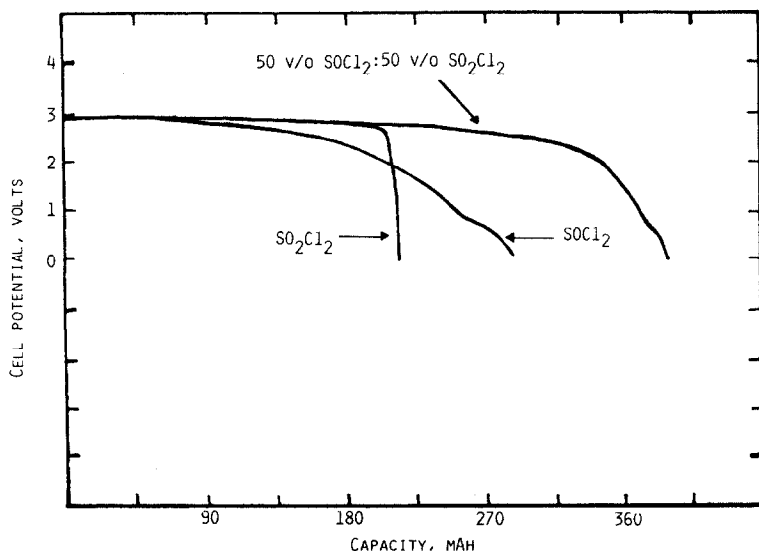


Fig. 7. Typical discharge curves for inorganic electrolyte cells at 5 mA cm^{-2} at $-30 \text{ }^\circ\text{C}$. The cathodes contain the same amount of carbon. The electrolytes contained 1 M LiAlCl_4 .

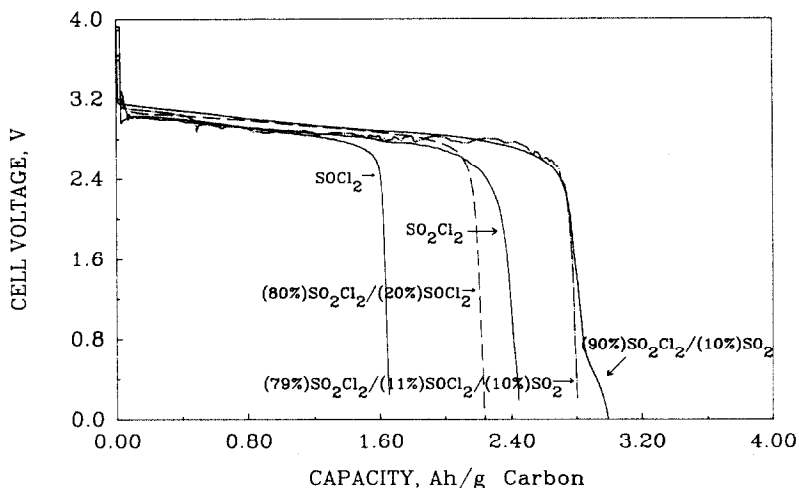


Fig. 8. Discharge performance of $\text{Li}/\text{SO}_2\text{Cl}_2$, Li/SOCl_2 , $\text{Li}/(\text{SO}_2\text{Cl}_2, \text{SO}_2)$ and $\text{Li}/(\text{SO}_2\text{Cl}_2, \text{SOCl}_2, \text{SO}_2)$ cells at room temperature and 10.0 mA cm^{-2} . LiAlCl_4 concentration = 1 M .

electrochemical couple. Nearly identical overdischarge behavior can be brought about in Li/SOCl_2 , Li/BCX , $\text{Li}/\text{SO}_2\text{Cl}_2$ and Li/CSC cells with certain initial Li to cathode ratios. The data presented below were obtained from a number of isolated studies and, consequently, they cannot be taken as results relevant to the most optimized cells of each category; rather the data should be used to assess certain general trends. Since forced overdischarge situations may be encountered by a single cell in a series-connected battery, a knowledge

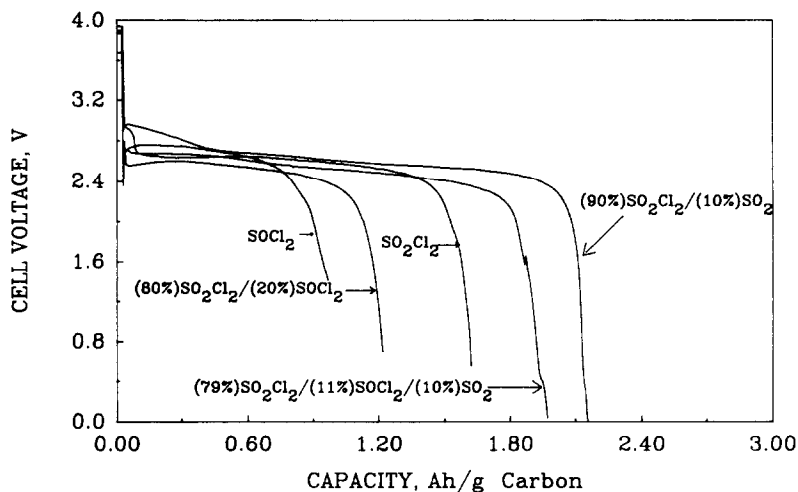


Fig. 9. Discharge performance of Li/SO₂Cl₂, Li/SOCl₂, Li/(SO₂Cl₂, SO₂) and Li/(SO₂Cl₂, SOCl₂, SO₂) cells at -20 °C and 10.0 mA cm⁻². LiAlCl₄ concentration = 1 M.

of the behavior of the cells under this operational mode is practically relevant. Readers are referred to the first systematic study of the overdischarge behavior of Li/SOCl₂ cells carried out by us in 1978 [48].

The individual electrode and cell potential profiles associated with the forced overdischarge behavior of cathode and Li-limited cells can be represented by the data presented in Figs. 3 and 4. Cathode-limited cells are usually characterized by small reversal voltages, with an ability to sustain this behavior for an indefinite period of time. The pressure-temperature profiles of the cell are determined by the discharge rate. The data in Fig. 3 exemplify the behavior of cathode-limited cells discharged and overdischarged at high rates. Under these conditions they can generate large amounts of heat and, consequently, high pressure. On the other hand, at low current densities of the order of 2 mA cm⁻² temperature increase and pressure buildup in cathode-limited cells were rather small [19]. Such cells exhibited safe behavior during prolonged overdischarge. Similar overdischarge profiles were shown by D-size Li/SOCl₂ and BCX cells. These latter data are presented in Figs. 10 and 11. It appears that during early stages of overdischarge, cathode-limited Li-oxychloride cells develop 'shorts' due to the dendritic Li plated on the cathode bridging across to the anode. Following shorting the cells seem to behave as a resistor, shunting the current without electrode polarizations.

Relatively low temperature rise and pressure buildup have been typically observed in Li-limited Li/SOCl₂ cells. This is illustrated by Fig. 4, as well as by other data reported in ref. 19. Based on the pressure-temperature profiles, Li-limited cells may be described as safer than their cathode-limited counterparts at high rates of discharge and forced overdischarge. The data in Fig. 12 depict the safe forced overdischarge behavior of D-size, Li-limited,

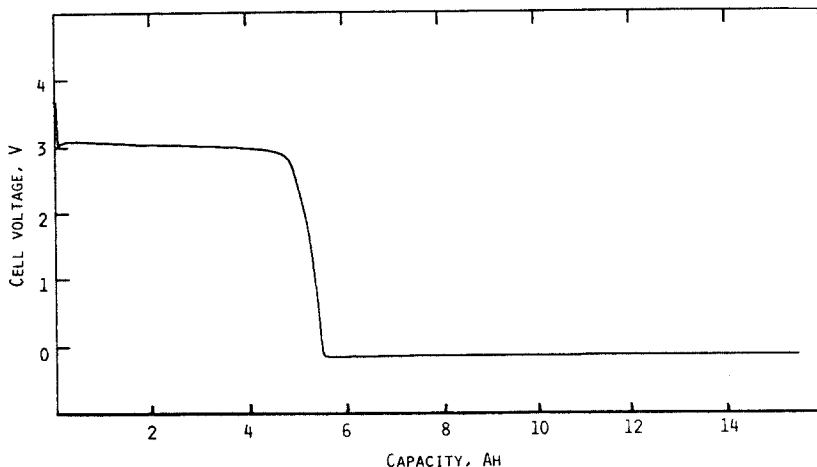


Fig. 10. Typical discharge/overdischarge curve of lithium/SOCl₂ cell at a constant current of 1.0 A. Li, 21 A h; SOCl₂, 18 A h; C, 5 g.

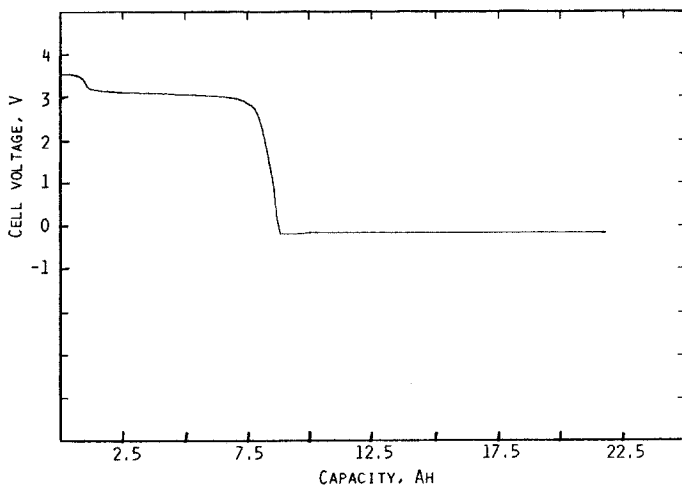


Fig. 11. Discharge and forced overdischarge behavior of a BCX cell at 1.0 A. Li, 21 A h; SOCl₂/BrCl, 18.1 A h; C, 5 g.

Li/SO₂Cl₂ + Cl₂' cells [44]. Li-limited Li/SO₂Cl₂ also exhibited similar behavior. The cell-voltage profiles of the Li/SO₂Cl₂ and Li/CSC cells during forced overdischarge are very similar to that in Fig. 4 for Li/SOCl₂ cells.

A third type of overdischarge behavior exhibited by Li/SOCl₂, Li/BCX, Li/SO₂Cl₂ and Li/CSC cells is illustrated in Fig. 13(a)–(c). The Li to liquid cathode ratios of these cells are also given for comparison. Their overdischarge is characterized by large negative fluctuations in voltages, and the cells, irrespective of the chemical couple, were prone to venting. We characterize these cells as anode-limited [48] because the large negative cell voltages

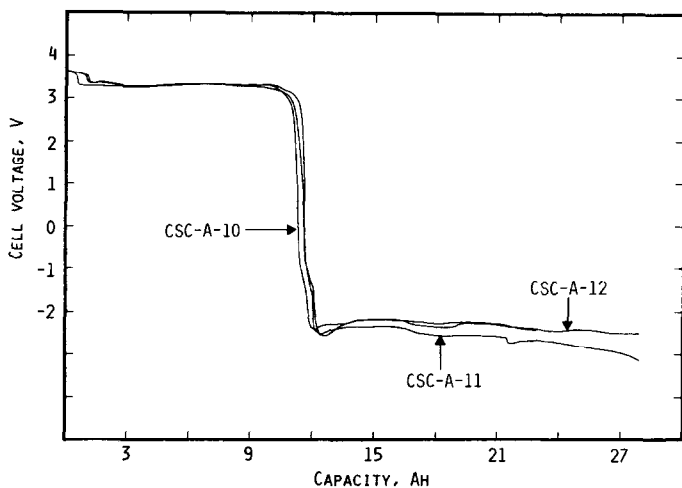
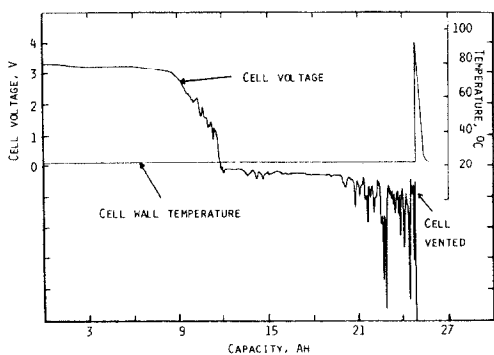


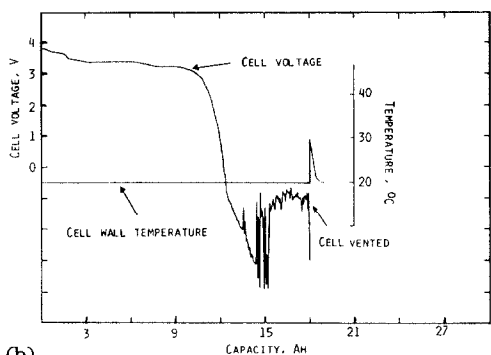
Fig. 12. Discharge and forced overdischarge behavior of an $\text{Li-SO}_2\text{Cl}_2 + \text{Cl}_2$ cell. Li, ~ 14 A h; $\text{SO}_2\text{Cl}_2 + \text{Cl}_2$, 18.2 A h; C, 4.7 g.

are caused by polarization of the anode towards positive values, yet in all cells small amounts of Li are still present on the anode grid. The Li seems to 'make and break' contact with the anode current collector grid causing the voltage to fluctuate. The anode voltage appears to fluctuate between Li potential and the oxidation potential of the electrolyte. Perhaps these fluctuations create hot spots on the anode with an ensuing runaway reaction and cell venting. Interestingly enough, we have found this behavior in four different Li-sulfur oxychloride cell chemistries, suggesting it as possibly a general behavior of Li-liquid cathode cells having certain Li-to-liquid-cathode ratios. The Li-to-cathode ratio prone to this behavior may vary from one type of cell to another, and may depend on cell designs also. Certainly, this type of forced overdischarge behavior must be avoided.

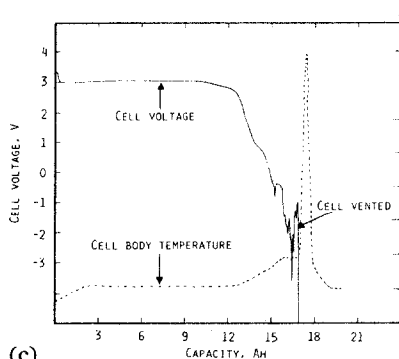
The pressure-temperature and potential profiles observed during resistive-load overdischarge of Li-sulfur oxychloride cells would be different from that experienced during forced overdischarge. Since the current in a constant load discharge substantially decreases as the voltage falls towards 0.0 V, cell heating would be much less [19]. The cathode would stay at a potential slightly positive of 0.0 V during the resistive load overdischarge. It has, however, been reported that if Li/SOCl_2 cells are overdischarged on resistive loads at low temperatures, e.g., -40 °C, and then warmed up to room temperature, they may explode [49]. It is possible that in such cells Li is underpotentially deposited on the cathode and it remains unpassivated at low temperatures. Upon warming the cell, this Li may react violently with SOCl_2 causing the explosions.



(a)



(b)



(c)

Fig. 13. Discharge and forced overdischarge behavior of Li-sulfur oxychloride cells. (a) Li/SOCl₂ cell. Current = 0.20 A. Li, 16 A h; SOCl₂, 18 A h; C, 5 g; (b) BCX cell at 0.2 A. Li, 16 A h; SOCl₂/BrCl, 18.1 A h; C, 5 g; (c) CSC cell at 2 A. Li, 20 A h; SO₂Cl₂/Cl₂, 16.7 A h; C, 4.7 g.

Voltage delay of Li-liquid cathode batteries

The same chemical reactions responsible for the formation of protective films on the Li anode making liquid cathode cells stable can also induce voltage delay. For example, during prolonged storage of Li/SOCl₂ cells, the LiCl film on the Li anode will become thick, and when the cell is subsequently discharged, it will experience a voltage drop proportional to the resistivity and thickness of this film [10]. Voltage delay, defined as the time it takes for the cell to attain a load voltage of ≥ 2 V, usually varies from seconds to hours depending on the type of cell, storage period, storage temperature, discharge load, and discharge temperature. The dissolution-precipitation mechanism responsible for increasing film thickness and voltage delay with storage has been illustrated earlier in reactions (11) and (12).

We have recently found that a desirable way to alleviate voltage delay is to use an Li⁺ conductive polymer electrolyte film as an overlayer on the Li anode. Particularly attractive polymer electrolytes for this application are those based on Li salt complexes of poly[bis-(methoxyethoxy-

ethoxide)phosphazene], called MEEP [50]. Room temperature ionic conductivities of several MEEP-based electrolytes measured by us are compared in Table 5 with those of the classical electrolytes based on poly(ethylene oxide), PEO. MEEP-based electrolytes are about 10 000 times more conductive than those based on PEO.

Figure 14(a) and (b) depicts how Li anodes with, and without, a polymer electrolyte overlayer would behave during storage of Li/SOCl₂ cells. The morphology depicted in Fig. 14(a) is based on the generally accepted model for LiCl growth on the Li anode.

A polymer electrolyte coating can be viewed as replacing the poorly conductive LiCl solid electrolyte ($> 10^{-8}$ ohm⁻¹ cm⁻¹) with a highly Li⁺ conductive interphase (10^{-5} – 10^{-4} ohm⁻¹ cm⁻¹) whose thickness would not change with storage. The representation in Fig. 14(b) is certainly one for an ideal case.

Lithium anodes coated with MEEP were heated for more than 2 months at 70 °C with little evidence of reaction between MEEP and Li. Voltage delay

TABLE 5

Conductivities of MEEP- and PEO-based electrolytes at 25 °C

Electrolyte	Conductivity (ohm cm) ⁻¹
MEEP · (LiClO ₄) _{0.25}	1.7×10^{-5}
MEEP · (LiSO ₃ CF ₃) _{0.25}	1.5×10^{-5}
MEEP · (LiBF ₄) _{0.25}	1.5×10^{-5}
MEEP · (LiAlCl ₄) _{0.25}	6.6×10^{-6}
PEO · (LiClO ₄) _{0.125}	5×10^{-9}
PEO · (LiBF ₄) _{0.125}	7×10^{-9}

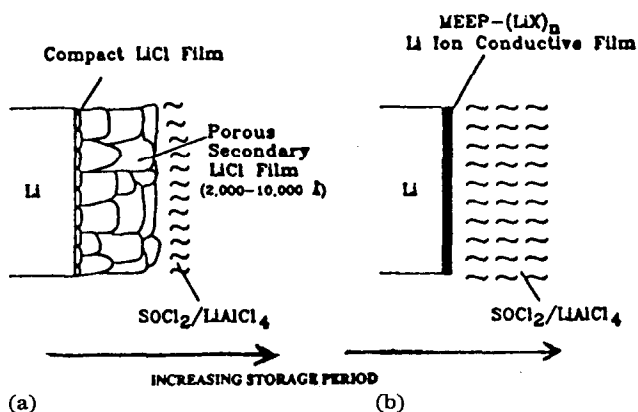


Fig. 14. (a) Schematic showing the voltage-delay-causing LiCl film at the Li surface. It consists of a compact, protective section, and a more porous secondary section whose thickness increases with the length of storage. (b) Lithium anode coated with an MEEP-(LiX)_n electrolyte on which the LiCl film does not grow.

studies of Li/SOCl₂ cells utilizing Li anodes coated with MEEP-(LiAlCl₄)_{0.25} or MEEP-(LiBF₄)_{0.25} showed voltage delays of less than 10 s when discharged at 10 mA cm⁻² at 20 °C after storage for 2 weeks at 70 °C. The ideal behavior depicted in Fig. 14 was not achieved in these initial studies. However, our present results suggest that MEEP-(LiX)_n and other Li⁺ conductive polymer electrolytes may be useful for alleviating the voltage delay of Li/BCX, Li/SO₂Cl₂, Li/CSC and other Li cells.

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References

- 1 C. R. Schlaikjer, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, New York, 1983, Ch. 13.
- 2 R. M. Murphy, P. W. Krehl and C. C. Liang, *Proc. 16th IECE Conf.*, 1981, p. 97.
- 3 C. C. Liang, M. E. Bolster and R. M. Murphy, *J. Electrochem. Soc.*, 128 (1981) 1631.
- 4 K. M. Abraham and M. Alamgir, *J. Electrochem. Soc.*, 134 (1987) 258.
- 5 A. N. Dey, H. C. Kuo, P. Piliero and M. Kallianidis, *J. Electrochem. Soc.*, 135 (1988) 2115.
- 6 P. H. Smith, S. D. James, K. M. O'Neill and M. H. Wilson, *J. Electrochem. Soc.*, 136 (1989) 1631.
- 7 K. H. Park, D. E. Stilwell, D. E. Bliss and M. H. Miles, in K. M. Abraham and B. B. Owens (eds.), *Materials and Processes for Lithium Batteries*, *Electrochem. Soc.*, Softbound Proc. Vol., PV89-4, (1989) 180.
- 8 R. D. Rauh, K. M. Abraham, G. F. Pearson and S. B. Brummer, *J. Electrochem. Soc.*, 126 (1979) 523.
- 9 H. Yamin and E. Peled, *J. Power Sources*, 9 (1983) 281.
- 10 E. Peled, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, New York, 1983, Ch. 3.
- 11 M. W. Rupich, L. Pitts and K. M. Abraham, *J. Electrochem. Soc.*, 133 (1982) 1307.
- 12 K. M. Abraham and L. Pitts, *J. Electrochem. Soc.*, 130 (1983) 1618.
- 13 K. M. Abraham and S. M. Chaudhri, *J. Electrochem. Soc.*, 133 (1986) 1307.
- 14 H. F. Bittner, *J. Electrochem. Soc.*, 136 (1989) 3147.
- 15 M. Anderson, *Spectroscopy*, 2 (1987) 54.
- 16 K. M. Abraham and L. Pitts, in A. N. Dey (ed.), *Lithium Batteries*, *Electrochem. Soc.* Softbound Proc. Vol., PV84-1 (1984) 265.
- 17 W. L. Bowden, L. Chow, D. L. DeMuth and R. W. Holmes, *J. Electrochem. Soc.*, 131 (1984) 229-233.
- 18 R. J. Mammone and M. Binder, *J. Electrochem. Soc.*, 134 (1987) 37.
- 19 K. M. Abraham, L. Pitts and W. P. Kilroy, *J. Electrochem. Soc.*, 132 (1985) 2301.
- 20 M. C. Dhamelincourt, F. Wallart, P. Barbier, G. Mairesse and P. Descroix, *J. Power Sources*, 14 (1985) 77.
- 21 W. Clark, F. Dampier, L. Lombardi and T. Cole, *Air Force Rep. No. AFWAL-TR-83-2083* (Dec. 1983).
- 22 A. N. Dey, *J. Power Sources*, 5 (1980) 57.

- 23 W. L. Bowden, J. S. Miller, D. Cubbison and A. N. Dey, in A. N. Dey (ed.), *Lithium Batteries*, Electrochem. Soc. Proc. Vol., PV84-1 (1984) 80.
- 24 K. M. Abraham and R. M. Mank, *J. Electrochem. Soc.*, 127 (1980) 2091.
- 25 K. M. Abraham, R. M. Mank and G. L. Holleck, in B. B. Owens and N. Margalit (eds.), *Power Sources for Biomedical Implantable Applications and Ambient Temperature Lithium Batteries*, Electrochem. Soc. Proc. Vol., PV80-4 (1980) 526.
- 26 B. J. Carter, R. M. Williams, M. Evans, Q. Kim, S. Kim, F. D. Tsay, H. Frank and I. Stein, in A. N. Dey (ed.), *Lithium Batteries*, Electrochem. Soc. Proc. Vol., PV84-1 (1984) 162.
- 27 T. Iwamaru and Y. Uetani, *J. Power Sources*, 20 (1987) 47.
- 28 L. R. Giattino, *U.S. Patent 4 262 065* (1981).
- 29 W. K. Behl, *Proc. 30th Power Sources Symp., Atlantic City, NJ, 1982*, p. 163.
- 30 K. A. Klinedienst, *J. Electrochem. Soc.*, 128 (1981) 2507.
- 31 M. Babai and U. Maishar, *Ger. Patent, 3 122 080* (1982).
- 32 N. Doddapaneni, *Proc. 31st Power Sources Symp., Cherry Hill, NJ, 1984*, p. 411.
- 33 F. Walsh and M. Yaniv, *ERADCOM Tech. Rep. DELET-TR-83-0386-F*, 1984.
- 34 A. Abelleira and F. Walsh, *Proc. 32nd Power Sources Symp., Cherry Hill, NJ, 1986*, p. 536.
- 35 W. P. Kilroy, M. Alamgir and K. M. Abraham, *Fall Meeting, Electrochem. Soc., Hollywood, FL, Oct. 1989*, Ext. Abstr. No. 78.
- 36 K. M. Abraham, M. Alamgir and W. P. Kilroy, *J. Power Sources*, 26 (1989) 597.
- 37 V. Feiman, E. Luksha and R. Bennet, in *Proc. 29th Power Sources Conf., Atlantic City, NJ, June 9-13, 1980*, The Electrochemical Society, Inc., Pennington, NJ, 1981, p. 59.
- 38 C. C. Liang, P. W. Krehl and D. A. Danner, *J. Appl. Electrochem.*, 11 (1981) 563.
- 39 P. W. Krehl and C. C. Liang, *J. Appl. Electrochem.*, 13 (1983) 451.
- 40 R. M. Murphy, P. W. Krehl and C. C. Liang, in *Proc. 16th Intersoc. Energy Conv. Eng. Conf., 1981*, p. 97.
- 41 K. M. Abraham and M. Alamgir, *J. Electrochem. Soc.*, 134 (1987) 2112.
- 42 K. M. Abraham, M. Alamgir and S. J. Perrotti, *J. Electrochem. Soc.*, 135 (1988) 2686.
- 43 W. D. K. Clark, S. J. Ebel, D. P. Eberhard and E. S. Takeuchi, *Proc. IECEC Conf., Denver, CO, 1988*, p. 1.
- 44 K. M. Abraham, M. Alamgir and R. K. Reynolds, *J. Electrochem. Soc.*, 135 (1988) 2917.
- 45 M. Binder, S. Gilman, W. L. Wade, Jr. and C. Walker, Jr., *J. Electrochem. Soc.*, 131 (1984) 1985.
- 46 K. M. Abraham and M. Alamgir, *J. Electrochem. Soc.*, 134 (1987) 258.
- 47 W. P. Kilroy, C. Schlijker, R. Yedmen, M. Alamgir and K. M. Abraham, *J. Power Sources*, submitted for publication.
- 48 K. M. Abraham, P. G. Gudrais, G. L. Holleck and S. B. Brummer, in *Proc. 28th Power Sources Symp., June 12-15, 1975, Atlantic City, NJ*, The Electrochemical Society, Inc., Pennington, NJ, 1979, p. 251.
- 49 C. A. Hayes, S. L. Gust, M. D. Farrington and J. A. Lockwood, in *Lithium Batteries*, Electrochem. Soc. Proc. Vol., PV87-1 (1987) 107.
- 50 K. M. Abraham, M. Alamgir and R. E. Reynolds, *J. Electrochem. Soc.*, 136 (1989) 3576.