

## THE Li-SOCl<sub>2</sub> CELL — A REVIEW

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### Summary

This review attempts to give a comprehensive, yet concise, introduction to the Li-SOCl<sub>2</sub> system: 138 references are included. It is hoped that most of the significant publications relating to the development of this cell have been included, and that the technological as well as the more fundamental aspects are covered.

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## Introduction

During the last 20 years lithium batteries have become significant electrochemical power sources. The increasing military and commercial requirements for light-weight, high-performance battery systems have led to the emergence of a range of cells based on lithium anodes [1]. Such requirements include high specific energy density for military and space programs, as well as requirements of long shelf life and miniaturization for electronic devices.

Lithium cell configurations are usually classified according to the nature of the cathode material, which may be either solid or liquid. Li-SOCl<sub>2</sub> cells belong to the latter class, since the solvent, or part of the electrolyte, also behaves as the active cathode reactant. The Li-SOCl<sub>2</sub> cell [2] consists of a lithium anode isolated from a porous carbon cathode by a separator. An electrolyte such as LiAlCl<sub>4</sub> is added to the SOCl<sub>2</sub> to increase the conductivity and to facilitate Li<sup>+</sup> ion transport.

## 2. Historical development

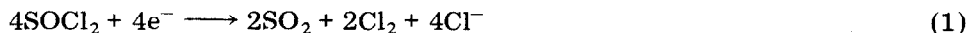
In 1969, Gabano [3] patented the use of SOCl<sub>2</sub> as a solvent for chlorine or bromine in a rechargeable lithium cell with 1.0 M LiAlCl<sub>4</sub> added as an electrolyte. He mentioned that important supplementary capacity could be obtained from the thionyl chloride, and that the products of reaction would be sulphur, sulphur dioxide and lithium chloride. It was noted that at lower rates such cells delivered almost twice the expected capacity based on the bromine present.

It was soon realised that SOCl<sub>2</sub> could perform well by itself as a depolarizer in a primary lithium cell. In 1972 a German patent [4] described such a cell in which the SOCl<sub>2</sub> was reduced at a porous carbon surface with LiAlCl<sub>4</sub> being added to the solvent.

By 1973, the Li-SOCl<sub>2</sub>-C cell was truly born; Auburn [5] and Behl [6] in separate communications described such a cell, along with other suitable oxyhalide depolarisers.

## 3. Cell reaction mechanisms

Before the development of the Li-SOCl<sub>2</sub> cell, Spandau and co-workers [7] studied the reduction of SOCl<sub>2</sub> solutions. They found that electrolysis was not possible in the poorly conducting pure solvent, but it could be carried out with the addition of 0.25 M (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NCl. The following scheme was proposed for the overall electrolytic reduction:

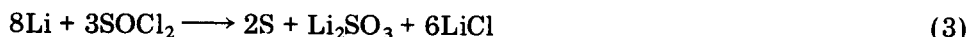


The formation of chlorine was not confirmed in later experiments. The cell reaction usually cited today, originally proposed by Gabano [3], for the Li-SOCl<sub>2</sub> cell discharge reaction is as follows:

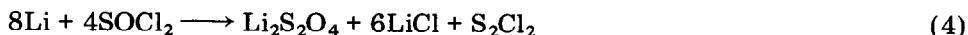


The reaction mechanism is thought to be rather more complex than this; various intermediates have been proposed. Other reaction stoichiometries have also been put forward.

Early work by Auburn [5] led to the following reaction being proposed:

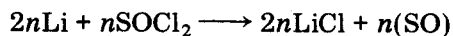


Li<sub>2</sub>SO<sub>3</sub>, detected by X-ray analysis, was thought to be formed rather than SO<sub>2</sub>, whose presence could not be confirmed. At the same time Behl [6] suggested that the SO<sub>2</sub> was reduced to Li<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and S<sub>2</sub>Cl<sub>2</sub>:



Later, however, the presence of SO<sub>2</sub>, neglected by the previous two reaction schemes, was positively confirmed. Quantitative analysis [8] showed the presence of LiCl, SO<sub>2</sub>, and elemental sulphur in discharged cells, but in relative quantities which did not correspond to any known reaction stoichiometry. Dey and Schlaikjer [9] noted internal pressure build-up in discharged C-sized cells, which were found by infra-red spectroscopy to contain SO<sub>2</sub>. They also confirmed the existence of sulphur crystals in the cells and the absence of sulphur oxyacid salts in the cathode. Beketaeva [10], after examining dried cathodes, confirmed that no S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup> or S<sup>2-</sup> was present.

Dey [11] proposed that reaction (2) represents the cell reaction which occurs via an unstable biradical SO which disproportionates to form SO<sub>2</sub> and elemental S. Marincic [12], however, maintained that there was insufficient SO<sub>2</sub> pressure in balanced Li-SOCl<sub>2</sub> cells to justify such a reaction. Schlaikjer and co-workers [13] confirmed that only a fraction of the SO<sub>2</sub> predicted from eqn. (2) is actually produced during the discharge. Dey's [11] proposed reaction, however, was essentially upheld, with slow decomposition of the unstable SO radical, thought to undergo polymerisation, occurring at the end of the discharge. The following two-stage reaction was proposed.



At least one sulphur oxyacid salt, thought to be Li<sub>2</sub>SO<sub>3</sub> was identified in cathodes from cells discharged at -20 °C. At this low temperature, a reaction such as (3), proposed by Auburn [5], and since discounted, was suggested. Results of a comprehensive qualitative analysis of 1.3 A h cells discharged at three different rates and at temperatures ranging from -50 °C

to 71 °C were reported by Baily and Kohut [14]. From their results these workers were confident that eqn. (2) summarised the overall cell discharge reaction at all temperatures, depths and rates of discharge investigated.

Behl [15] carried out a study of the electrochemical  $\text{SOCl}_2$  reduction by cyclic voltammetry at a glassy carbon surface. A large reduction peak, thought to correspond to eqn. (2) was identified with no corresponding anodic peak, indicating an irreversible reaction. He concluded that if any SO radical species existed, it was unstable and quickly disproportionated. No evidence for further reduction of  $\text{SO}_2$  was found. Venkatesetty [16] carried out the analysis in solutions of  $\text{SOCl}_2$  in dimethylformamide and dimethyl sulphoxide. He identified three reduction peaks, thought to be due to a two-stage  $\text{SOCl}_2$  reduction process via an  $\text{SOCl}^\cdot$  radical, followed by  $\text{SO}_2$  reduction.

From another cyclic voltammetric study of  $\text{SOCl}_2$  reduction in various organic solvents and supporting electrolytes, Bowden and Dey [17] proposed the following, one electron steps



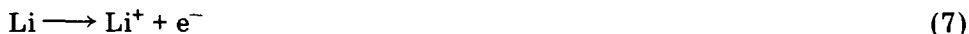
Again, as discussed previously, the SO radical subsequently decomposes. Towards the end of the reaction, dimerisation and polymerisation of SO is likely, as proposed by Schlaikjer [13]. Immediate polymerisation of the SO radical is further substantiated by there being very little experimental evidence for the existence of the intermediate and, although the presence of SO and  $\text{S}_2\text{O}$  have been indicated by infra-red analysis [18], the stability of both is thought to be low.

Analyses of cyclic voltammograms show a substantial dependence of peak potential on scan rate, indicative of the irreversible character of  $\text{SOCl}_2$  reduction. A plot of peak height *versus* the square root of scan speed was linear, passing through the origin, indicating a diffusion controlled process [19, 20]. At lower overpotentials [20], however, the reduction is thought to be kinetically controlled, a transition to diffusion control occurring with increasing overpotential. At potentials more negative than +2.7 V mass transport processes were thought to govern all cell reactions occurring, the controlling factor being the nature of the LiCl film on the electrode.

Other species thought to take part in the reaction at some stage have also been proposed. Venkatesetty and Saathoff [21], using cyclic voltammetry to study the reduction of an  $\text{SOCl}_2$ -1.8 M  $\text{LiAlCl}_4$  solution at a glassy carbon surface, found peaks corresponding to chlorine and sulphur dioxide. The chlorine was thought to form by the dissociation of  $\text{SCl}_2$ . Intermediates such as  $\text{SCl}_2$ ,  $\text{Cl}_2$  and  $\text{OCIS}$  [22 - 24] have been identified in cells, leading to more complex cell reaction mechanisms [24, 25] being suggested.

#### 4. The anode

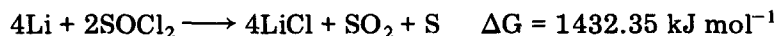
Lithium has many advantages as a battery anode material; it is mechanically strong, has a low equivalent weight, and the highest equilibrium potential of any metal. In Li-SOCl<sub>2</sub> cells the negative electrode consists of lithium foil pressed onto an expanded nickel screen, or cold bonded with stainless steel, aluminium or zinc, which acts as a current collector. The anode is closely packed in a cell facing a porous carbon cathode, from which it is isolated by a piece of separator material. Under such conditions anodic oxidation proceeds uniformly over the surface, even at high current density (> 200 mA cm<sup>-2</sup>), according to the following process:



The theoretical capacity based on the weight of the anode is never achieved [26]. This is thought to be because of lithium corrosion at low rates and some sort of mechanical erosion at higher rates. The anode is not usually regarded as the performance limiting electrode, since passivation of the carbon cathode by insulating LiCl is generally the reason for cell failure [27, 28]. Under certain conditions, however, lithium is anodically passivated in SOCl<sub>2</sub> solutions at room temperature [29, 30]. Anode passivation is associated with the accumulation of anodic dissolution products in the pores on the surface layer of the metal, and has been found to limit the utilisation of the lithium electrode at high current densities. Abraham and co-workers [31] also concluded that anode polarization may terminate the end of discharge, and that anode-limited cells were not necessarily the same as lithium-limited cells.

##### 4.1. Film formation

The kinetic stability of lithium in many organic solvents has been known since the 1960s. This is due to a film which forms on the lithium surface, preventing further lithium dissolution which would otherwise result from its thermodynamic instability, *e.g.*, for lithium thionyl chloride:



This film has been extensively studied for a number of battery electrolytes [32 - 47] and its growth mechanism and effect on battery performance have been evaluated. It forms immediately the electrode and electrolyte are in contact and grows continually with storage time [40] and temperature [36]. A variety of methods exists for monitoring the film thickness and growth rate. These include the examination of SEM photographs of cross sections of lithium electrodes [32, 36] and by measuring the weight gain during storage in the electrolyte solution [34]. Micropolarization measurements on a lithium electrode also allow determination of the interfacial capacity, from which the film thickness can be calculated using a parallel plate capacitor equation [38, 39]. A.C. impedance measurements on lithium electrodes have led to an easy, reproducible method for monitoring the surface film in SOCl<sub>2</sub>-based electrolyte solutions [42, 43].

Peled [38, 44] described the film as a solid electrolyte interphase (SEI), since it acts as an interphase between the electrode and solution, having the properties of a solid electrolyte. Ideally, SEIs should not allow electron transfer, but a large number of Schottky lattice defects allow  $\text{Li}^+$  ion transfer through the film. Growth of the film has been shown to occur by ionic migration and diffusion in the film [32, 34, 35]; the rate of increase of this SEI approximates to a parabolic growth law. The rate of film growth on a lithium electrode in  $\text{SOCl}_2$  is greater for more concentrated  $\text{LiAlCl}_4$  solutions and increases with temperature [32, 36]. The size of the  $\text{LiCl}$  crystals [36] have also been demonstrated to increase with temperature. This may, however, only be true up to  $130^\circ\text{C}$ , after which the crystal size decreases, possibly due to a greater quantity of  $\text{SO}_2$  present in the electrolyte [45].

It is widely believed that the  $\text{LiCl}$  film consists of two layers [33 - 35, 45, 46]. The first is a thin, compact film which forms immediately the electrode and electrolyte make contact, while on top of this is a thicker layer of porous, non-insulating  $\text{LiCl}$ , which grows continually with time. It has also been suggested that there may be three layers [47].

#### 4.2. Voltage delay and its alleviation

The voltage delay phenomenon occurs when a lithium cell is discharged after a prolonged period of storage. Cell voltage at the start of the discharge is lower than expected, and increases slowly with time. This effect is caused by a passivating film which forms on the anode [33]. Dey [36] demonstrated that this was an anode effect by measuring the potential-time behaviour for several lithium specimens after storage for various times in an electrolyte solution. The voltage against a lithium reference electrode after galvanostatic, anodic polarization was measured and found to rise slowly from an initially low value. As the electrode is polarized the film breaks up due to slow mechanical disruption caused by dissolution of lithium from underneath the film.

The anode and electrolyte solution purities have been shown to be an important factor in controlling the voltage delay problem [8, 48]. For example, iron in the electrolyte has been shown to increase the rate of film growth, causing a much thicker film to form with increased voltage delay [48]. Driscoll [8] found that storing the electrolyte solution over lithium metal at  $71^\circ\text{C}$  removed  $\text{Fe}$ ,  $\text{Cu}$ ,  $\text{HCl}$ , and hydroxyaluminium compounds which are reactive to lithium. Cells using electrolyte purified in this manner showed no voltage delay until after 208 hours of storage.

Alloying lithium with other metals such as silver (1%) and magnesium has been carried out in an attempt to alleviate voltage delay [8]. Calcium was found to be the best alloying agent [49]; it is thought to act by plating onto the anode surface, making it more resistant to passivation than lithium.

Chua and Merz [50], after finding that the voltage delay was less for partially discharged cells, showed that it could be significantly reduced by doping the electrolyte with about 5%  $\text{SO}_2$ . Additions of greater than 10%

SO<sub>2</sub>, however, aggravated the problem. Dey [32] showed that SO<sub>2</sub> in the electrolyte caused the passive film to acquire a more orderly appearance and reduced corrosion. Other inorganic additives may also help to reduce voltage delay [51].

Additions of PVC to the electrolyte have also had the effect of reducing voltage delay [48, 52]. PVC is thought to act by coating the lithium surface thereby creating a different crystal morphology with larger pores and tunnels, facilitating Li<sup>+</sup> ion transport. Cyanoacrylate coatings on lithium [53] improve voltage delay in Li-SOCl<sub>2</sub> cells, although it is not certain whether they merely provide a physical barrier to LiCl film formation, produce a slowly formed film of different morphology, or control crystal growth from the electrolyte.

Shlaikjer [54, 55] proposed the use of thionyl chloride electrolytes containing B<sub>10</sub>Cl<sub>10</sub><sup>2-</sup> and B<sub>12</sub>Cl<sub>12</sub><sup>2-</sup> as replacements for the commonly used LiAlCl<sub>4</sub>. He showed that using such electrolytes the voltage delay problem was lessened [56], probably due to the smooth structure of the passivating layer on the lithium electrode in the polyhedral borane electrolyte. Dey showed that relatively small quantities of closoborane anions in the electrolyte significantly reduce voltage delay [57, 58]. SEM pictures showed that the anode film consisted of uniformly grown small crystals. Gabanao [59, 60] claims that an electrolyte made by dissolving either Li<sub>2</sub>O or Li<sub>2</sub>S in an AlCl<sub>3</sub>-SOCl<sub>2</sub> solution has superior voltage delay characteristics, although capacity is somewhat reduced.

## 5. The cathode

The cathode substrate in Li-SOCl<sub>2</sub> cells provides a conductive surface on which SOCl<sub>2</sub> is depolarized. This inert electrode is usually made from amorphous carbon powder with a PTFE binder, the filamentary nature of which minimises blockage of the active carbon surface [61]. The most commonly used carbon is acetylene black, which consists of submicron sized particles produced by thermal or oxidative vapour phase decomposition of hydrocarbons [62]. Cathodes are usually prepared by pasting a carbon/PTFE mix onto an expanded nickel current collector and pressing [6, 62]. Auburn used hot pressing at 200 psi for three minutes [5]. Another procedure entails rolling the carbon/PTFE mix onto the current collector [11, 63]. During cell discharge SOCl<sub>2</sub> reduction takes place at such a cathode, resulting in the precipitation of reaction products, mainly LiCl, within the pores of the substrate. This leads to eventual passivation of the cathode surface and, hence, cell failure. Much of the Li-SOCl<sub>2</sub> cell research undertaken is to improve the performance of this positive electrode.

### 5.1. Optimisation of cathode performance

#### (a) Type of carbon

The properties of manufactured carbons vary according to the precursor, as well as the manufacturing procedure. Shawinigan Acetylene Black

(SAB) is the most widely used form for Li-SOCl<sub>2</sub> cathodes, as it was initially found to give the highest coulombic capacity [6, 64]. Dey, after examining twelve carbon types, found that particle size, BET surface area, and density did not greatly affect cell performance, most performing as well as SAB [61]. Wade and co-workers in a later study found that two other carbons, namely, Cabot CSX-179B and United Carbon XC-6310, both having a high surface area, displayed less cathode polarization and had a much greater capacity than SAB [65, 66] in Li-SO<sub>2</sub>Cl<sub>2</sub> cells.

In a recent study by Klinedinst [67], nine different carbon blacks were compared. He considered their ability to accommodate solid discharge products with minimum resistance losses and their ability to behave as heterogeneous catalysts for the cathodic half-cell reaction. Of the commercially available carbon blacks examined, Ketjenblack EC (surface area 1000 m<sup>2</sup> g<sup>-1</sup>) and Black Pearls 2000 (surface area 1050 m<sup>2</sup> g<sup>-1</sup>) displayed high capacity and load voltages. They gave almost twice the capacity of SAB (surface area 60 m<sup>2</sup> g<sup>-1</sup>).

It is possible to use materials other than carbon as current collector cathodes, *e.g.*, nickel [68] has been proposed as an alternative to carbon for low rate cells.

#### *(b) Cathode structure*

Klindedinst concluded that the porosity of the carbon black material has an important bearing on the Li-SOCl<sub>2</sub> cell capacity [67]. The porosity is, in turn, more directly related to the dibutyl phthalate absorption of the cathodes (cm<sup>3</sup>/100 g), than the surface area as defined by iodine absorption (m<sup>2</sup>/g). Other workers have also found that the cell capacity is related to the pore volume of the cathode [64, 69]. Danel and co-workers [70] concluded that the pore-size distribution in carbon cathodes was very important since small pores are quickly blocked and give little capacity. The distribution results from carbon black manufacturing processes and characteristics. The addition of pore-formers has also been successfully used to improve the pore size distribution within the cathode [67]. Finely-divided (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and NH<sub>4</sub>HCO<sub>3</sub> were added to the cathode and subsequently removed by thermal decomposition.

The pre-treatment of carbon cathodes with acetone has led to an increase in cell voltage and capacity for Li-SO<sub>2</sub>Cl<sub>2</sub> cells [65, 66] and Li-SOCl<sub>2</sub> cells [71]. This treatment is thought to work by removing impurities from the carbon and increasing the total pore volume and average pore diameters.

Provision should be made in the cell for electrode swelling during discharge, since this has been shown to increase electrode capacity by up to 33% due to an increase in cathode porosity [64, 72 - 74].

PTFE is used as an inert binder in the cathode, giving mechanical stability. Dey [11] found that a 10% w/w PTFE addition was necessary to bind the carbon particles together; more than this reduced the capacity by physically restricting the active surface. Other workers, however, con-



cluded that up to 50% PTFE may be used without unduly affecting the cathode efficiency [70] since the pore size distribution is not greatly affected by the PTFE content. Binders other than PTFE have been used. For example, chlorinated hydrocarbons have been identified as an alternative: these have low contact angles and good chemical stability in the electrolyte [75]. These elastomer-bonded carbon electrodes contained a different pore structure and were found to have 100% greater capacity than PTFE-bound electrodes at high current density.

The thickness of the cathode is also critical. Cathodes which are too thick are under-utilized at high current density, as demonstrated by Dey and Bro [27, 76] using depth profile analysis. In terms of capacity per unit mass or volume of cathode material, thinner cathodes have a greater rate capability [77, 78]. A mathematical study by Pollard and co-workers [79, 80] suggests that the reaction distribution in porous carbon cathodes is predominantly towards the front face of the electrode, nearest to the anode. EDAX analysis of discharged cathodes confirms this [73].

### *(c) Electrocatalysts*

The use of carbon in commercial cells arises from its availability and cheapness. The performance of carbon cathodes is, however, further enhanced by the addition of other materials which have a catalytic effect on the cell performance. Substantial increases in cell operating voltage and discharge capacity have been achieved by using finely-divided platinum in the cathodes [78]. As little as a 1% w/w addition of platinum is sufficient to increase cell performance greatly. Such small quantities were thought to be economically viable. Copper powder additions to the cathode have been found to increase the performance and safety of Li-SOCl<sub>2</sub> cells [81]. The increase in safety was thought to be due to copper reacting with sulphur produced in the cell reaction which would otherwise react explosively with lithium. Behl [82] showed that, in SOCl<sub>2</sub>, copper is oxidised to copper(II) chloride which, during the cell reaction is reduced to copper(I) chloride before subsequent re-oxidation. Other pure metals have been found to have a catalytic effect in Li-SOCl<sub>2</sub> cell performance, including iron [83], silver and palladium [84].

Transition metal phthalocyanines, successfully employed as catalysts for fuel cell cathodes, also increase the performance of Li-SOCl<sub>2</sub> cells. Doddapaneni, after comparing eight organometallic complexes as possible catalysts, found cobalt and iron phthalocyanines to be the most effective [85]. Other workers have since confirmed this [74], although these catalysts have been found to be less effective at higher temperatures [71]. The way in which these catalysts function is complex and not fully understood but, in many instances, they are thought to alter the reaction mechanism [86, 87]. Halogens have also been used as electrocatalysts [88, 89], although they are added to the electrolyte solution and do not affect the cathode structure.

#### (d) Temperature

As the temperature is increased, the capacity of the Li-SOCl<sub>2</sub> cell increases, due to greater cathode utilisation [77]. This is attributed to an increased solubility of reactants and products, improved efficiency of LiCl deposition, and increased electrolyte conductivity. Although most workers agree with this, some found a decrease in cathode efficiency beyond 23.9 °C — thought to be due to a parasitic reaction between SOCl<sub>2</sub> and S [90].

The low freezing point of SOCl<sub>2</sub> (−104.5 °C) has favourable implications for Li-SOCl<sub>2</sub> cells at low temperatures. At sub-zero temperatures, however, there is a loss in capacity [91, 92] and a higher cell polarization [67, 91]. This has been attributed to an increase in the precipitation of elemental sulphur which is less soluble than at ambient temperature [66]. Some of the capacity is, however, recovered on warming. It is likely that two temperature regions exist, each with different thermodynamic characteristics [19].

### 6. The electrolyte solution

The addition of a suitable electrolyte to SOCl<sub>2</sub> is necessary in order to increase its conductivity and to facilitate Li<sup>+</sup> ion transport. LiAlCl<sub>4</sub> is usually employed, probably because of its reasonable solubility in SOCl<sub>2</sub> and its relative cheapness. Dey [11] found that the intrinsic capacity of Li-SOCl<sub>2</sub> cells was a function of the electrolyte concentration, with 1.0 M LiAlCl<sub>4</sub> being optimum. He later suggested that for high rate cells, higher concentrations of electrolyte were preferable, 1.8 M being the optimum [27, 93]: this is still generally regarded as so today [94].

The presence of free AlCl<sub>3</sub> in the electrolyte solution can result in higher cell voltages and increased capacity [77, 95 - 97]. AlCl<sub>3</sub>, a Lewis acid, is thought to react with the chloride ions formed as a result of SOCl<sub>2</sub> reduction, and therefore delay LiCl precipitation. 3.0 M AlCl<sub>3</sub> was found to be an optimum concentration for cells employing thick carbon cathodes, with 4.5 M AlCl<sub>3</sub> being more effective for thinner ones (37 μm) [77, 95]. Such an electrolyte solution, however, is restricted to reserve cells which will be considered further in a subsequent section.

As discussed previously, alternative electrolyte salts with closoborane anions reduce the voltage delay problem in Li-SOCl<sub>2</sub> cells [54 - 58], as do salts containing Li<sub>2</sub>O and Li<sub>2</sub>S [60, 98]. Auburn [99] reported that other than BCl<sub>3</sub> solutions, group 3b chlorides in SOCl<sub>2</sub> dissolve LiCl. LiGaCl<sub>4</sub> and Li<sub>2</sub>O·2GaCl<sub>3</sub>, when used as electrolytes in Li-SOCl<sub>2</sub> solutions, have shown a similar conductivity and solubility to LiAlCl<sub>4</sub>, but yield 60% greater capacities [100].

Electrolyte purity is important [11, 57]; better battery performance has been obtained from laboratory-prepared electrolyte. Purification methods include refluxing with lithium metal after distillation [101], and

distillation after pre-treatment with triphenyl phosphate, to remove sulphur containing impurities [5, 13].

Szpak and Venkatasetty [102 - 105] have undertaken an extensive study of the properties of  $\text{SOCl}_2$  electrolytes containing  $\text{AlCl}_3$  and  $\text{LiCl}$ . Conductance, viscosity, and density data for these solutions have been obtained and analysed for a range of temperatures and compositions. Effects of dissolved  $\text{SO}_2$  have also been investigated. The results are interpreted in terms of ion-solvent and ion-ion interactions, and should be of interest to battery technologists.

## 7. Battery design, performance and applications

$\text{Li-SOCl}_2$  cells have one of the highest energy densities of all commercial battery systems ( $500 \text{ W h kg}^{-1}$ ) together with a high cell voltage, long shelf life, and good, low-temperature performance. This has led to many proposed and existing applications, ranging from low rate cells for medical implants to super high rate batteries for military use. For convenience in the ensuing discussion the systems will be classified according to their rate capability.

### 7.1. Cells for low rate applications

These are usually AA size, AAA size or small D cells, used for implantable cardiac pacemakers [106, 107] where they have an excellent reliability record. Recently,  $\text{Li-SOCl}_2$  cells have also found application in micro-electronics for CMOS memory preservation [52].

The "bobbin", or concentric electrode structure, is a simple, popular design. This structure comprises a cylindrical cell in which one electrode is attached to the wall of the container and completely surrounds the other. One such design allows a central hollow volume for additional electrolyte, since there is sufficient space within the cathode pores to accommodate all of the electrolyte solution [12, 108]. The rate capability of a bobbin cell is enhanced by using two concentric cylindrical anodes with a carbon cathode in between [26].

### 7.2. Intermediate cells

Attempts to scale bobbin construction to any cell larger than a D size results in a poor performance [109]. The rate capability can, however, be greatly enhanced using a spirally wound structure which increases the surface area of the electrodes. Cell construction involves winding a pair of flat, strip electrodes, with separators, around a mandrel and placing it in a cylindrical container, which acts as one terminal. The terminal to the other electrode is fed through a glass-to-metal seal incorporated as part of the cover assembly in hermetically-sealed cells. Optimum design of such cells has been achieved through computer modelling [109, 110]. Dey has carried out a number of studies on C and D sized wound structures [11, 27, 28, 76].

Using an empirical approach, it was shown that about  $3.3 \text{ A h g}^{-1}$  of carbon was the maximum possible capacity which could be obtained using a wound geometry. It was also demonstrated that most of the reaction at high currents is localised near the cathode tab, making the cell wall the hottest part on shorting. A flat, cylindrical cell has been described in which 35 disc-shaped anodes and cathodes, with glass separators, were stacked in parallel. This arrangement was able to provide high power in pulsed and continuous mode [111].

### 7.3. High capacity cells

Large Li-SOCl<sub>2</sub> cells usually employ prismatic structures with parallel electrodes [110]. Partly because of safety hazards associated with such a high-powered system, however, commercial applications are limited and the major uses are military [112].

Batteries of 10 000 A h are currently installed in 'Minuteman' missile silos, in parallel with lead-acid batteries [113]. Load sharing between the two batteries allows for a smooth transition between the two systems with no voltage delay effects, the lead-acid system initially taking most of the load. Very-high-rate batteries have been developed, including a 16 500 A h system [114], and many other examples of high capacity batteries are cited in the literature.

High-rate cells are used for many naval and undersea applications such as mines, aids to navigation, submerged sonobouys, portable communications, missiles and torpedos [115].

### 7.4. Reserve cells

A reserve cell is one in which the electrolyte is maintained in a separate compartment from the main electrode stack and is only admitted as power is required. Such cells avoid problems with voltage delay, which may be critical for high rate applications where the overall discharge time is a few minutes. Reserve cells also give an almost indefinite shelf life, which makes them ideal for standby power applications. Many reserve cells use free Lewis acid in the electrolyte in order to increase cell discharge times [77]. Actual concentrations of aluminium chloride are rarely quoted, although an electrolyte based on 3.0 M AlCl<sub>3</sub> has been found to give good performances [77, 116].

A major design problem which exists with reserve batteries involves activation. Small, low-rate reserve cells have been designed in which the central reservoir of electrolyte is held in a glass ampoule which could be broken by striking the bottom of the cell [117, 118]. In some instances activation may take advantage of the application. For example, a reserve cell used to power an artillery-delivered communications device is activated by the high spin rate encountered as the device is fired [116]. More usually, a more cumbersome means of activation is employed, the electrolyte being forced into the electrode stack by means of a gas generator as power is required [97, 119].

## 8. Safety of Li-SOCl<sub>2</sub> cells

In spite of the many performance advantages of Li-SOCl<sub>2</sub> cells, questions still remain relating to the hazardous nature of the cell. A few widely publicised incidents of cells exploding when abused, or venting to evolve noxious gases, have led to a general wariness. The major safety hazards of these cells are overheating during, and after, discharge, pressure build-up, abuse, and hazards during cell reversal. The reasons for each of these is briefly examined.

### 8.1. Heat generation

Although an increase in temperature can improve the performance of Li-SOCl<sub>2</sub> cells, excessive heat production in the cell is a safety hazard. Much of the heat generated arises from chemical reactions both during, and after, the cell reaction, as S radical species are converted to SO<sub>2</sub> and S [120, 121]. Internal ohmic heat generation is considerable during cell discharge, and in one example was calculated to be 37.3 kW, with 120 kW of total electrical output [122]. Additional heat generation is likely with cells containing an excess of AlCl<sub>3</sub> in the electrolyte [123]. This is due to the anode corrosion reaction and an entropy increase during the transition from the acidic reaction to the reaction in neutral electrolyte, producing LiAlCl<sub>4</sub> [124].

As the temperature increases there are several safety hazards, the electrolyte boils, the sulphur melts and, if the temperature is raised sufficiently, the lithium melts. Marincic [122] calculated that for a 90 kg, high rate, Li-SOCl<sub>2</sub> battery all of the safety hazards would be encountered unless external cooling of the battery was provided, although all the stored energy should be exhausted before the lithium melts. Excessive heat generation, causing the cell temperature to approach the melting point of lithium, results in what is known as thermal runaway conditions [125]. It is likely that a critical size of cylindrical, high-rate Li-SOCl<sub>2</sub> battery exists, below which external cooling is not necessary, although other factors such as cell geometry and materials of construction are important [126]. Mathematical predictions show that a high rate torpedo battery can only be stable under certain limiting conditions and with flowing electrolyte [127]. Advances in design should improve heat dissipation in cylindrical batteries [128].

### 8.2. Internal pressure build-up

This is likely to occur directly as a result of a build-up of SO<sub>2</sub> within the cell, due to a decrease in solubility of SO<sub>2</sub> in the electrolyte with temperature [122]. This internal pressure could become critical [90], and therefore most cells require a safety vent. Dey showed that such a vent needs to respond to relatively low pressures in order to prevent explosion [28], and proceeded to develop a truly hermetic, reliable, low-pressure vent, resistant to external abuse [129].

### 8.3. Abuse

The major 'accidental' abuse conditions likely to occur in Li-SOCl<sub>2</sub> cells are short-circuiting and charging. The former may result in thermal runaway conditions or explosions [125], but can usually be prevented by the use of fuses, semi-conductor devices or relays [130]. Charging hazards, although not thought to be major [131], can usually be prevented by incorporation of a safety diode [130].

The results of numerous electrical and mechanical abuse tests on Li-SOCl<sub>2</sub> cells are to be found in the literature, as attempts to improve safety are carried out. Small, low-rate cells are generally regarded as reasonably abuse resistant [132, 133].

### 8.4. Hazards during cell reversal

At the end of discharge, cell voltage reversal is a likely condition in high rate battery stacks and is potentially explosive. This may occur in anode limited cells when depletion of lithium from the negative electrode forces other oxidation reactions to occur at this electrode, or in cathode limited cells in which polarization of the SOCl<sub>2</sub> reduction process causes lithium deposition on the positive electrode [134]. There is debate concerning the relative safety of anode and cathode limited cells. Some claim that cathode limited cells are safer, since in anode limited cells explosions are possible due to sensitive substances produced by oxidation of materials present in the cell [31, 133]. Others, however, maintain that anode limited cells, in which the lithium is exhausted just prior to cathode failure, are safer. In cathode limited cells heating may cause any remaining lithium to melt. Further, less heat is evolved in anode limited cells, since cathode polarization is lower [135]. There is also less potential for a hazardous reaction between lithium and sulphur [90]. It must be borne in mind that anode limited and lithium limited may not be the same since, under certain circumstances, anode polarization may cause the end of cell life [29 - 31]. A 'balanced' cell composition in which cell reactants are exhausted simultaneously is thought to show good safety characteristics on voltage reversal [136]. A ceramic separator, when employed in place of a porous alumina/silica based separator, has been demonstrated to reduce hazards on voltage reversal [137]. Internal and external switching devices have also been proposed to overcome this hazard [138].

## 9. Conclusions

Since its almost accidental conception in the early 1970s, the Li-SOCl<sub>2</sub> cell has had a major impact on the battery industry: in particular speciality batteries. These take advantage of the long shelf life, very high energy density, and good low temperature performance of this battery system. Hence, diverse applications exist ranging from implantable cardiac pace-makers to torpedoes, to CMOS memory preservation, to arctic sonobuoys.

Because the cathode appears to be the performance limiting electrode, much recent research has centred around improving the capacity of this carbon positive electrode by the addition of electrocatalysts and the use of alternative morphological forms of carbon powder. Improvements in performance obtained by using these methods are likely to eclipse the advantages of acid electrolytes. It is also likely that a good performance-yielding type of carbon is preferable to electrocatalysts, which are often expensive and may decompose either on storage or at elevated temperature.

Voltage delay is often a serious problem in Li-SOCl<sub>2</sub> cells and it is important that an effective solution to this problem is successfully developed for commercial batteries.

The high performance of these batteries should lead to increasing applications, particularly for the domestic market. However, they must first be demonstrated to have a high level of safety, with allowance made for abuse.

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