LIQUID CATHODE PRIMARY BATTERIES

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Summary

Lithium/liquid cathode/carbon primary batteries offer from 3 to 6 times the volumetric energy density of zinc/alkaline manganese cells, improved stability during elevated temperature storage, satisfactory operation at temperatures from −40 to +150 °C, and efficient discharge at moderate rates.

The lithium/sulfur dioxide cell is the most efficient system at temperatures below 0 °C. Although chemical reactions leading to electrolyte degradation and lithium corrosion are known, the rates of these reactions are slow. While the normal temperature cell reaction produces lithium dithionite, discharge at 60 °C leads to a reduction in capacity due to side reactions involving sulfur dioxide and discharge intermediates.

Lithium/thionyl chloride and lithium/sulfuryl chloride cells have the highest practical gravimetric and volumetric energy densities when compared with aqueous and most other nonaqueous systems. For thionyl chloride, discharge proceeds through a series of intermediates to sulfur, sulfur dioxide and lithium chloride. Catalysis, leading to improved rate capability and capacity, has been achieved. The causes of rapid reactions leading to thermal runaway are thought to be chemical in nature. Lithium/sulfuryl chloride cells, which produce sulfur dioxide and lithium chloride on discharge, experience more extensive anode corrosion. An inorganic cosolvent and suitable salt are capable of alleviating this corrosion.

Calcium/oxyhalide cells have been studied because of their promise of increased safety without substantial sacrifice of energy density relative to lithium cells. Anode corrosion, particularly during discharge, has delayed practical development.

Introduction

Normal temperature non-aqueous cells in which the liquid component of the electrolyte acts both as the solvent and the oxidant or active cathode material have been identified and developed over the past fifteen years. The principle of operation, now familiar, is that during discharge the solvent is

reduced on a conductive surface, usually on acetylene or other carbon black with 5 - 10% of Teflon as a binder. The porosity of the carbon matrix is usually about 80% for operation at low to moderate rates, that is, below about 10 mA/cm^2 of apparent cathode surface area. The anode, usually lithium, calcium, or an alloy, is protected from extensive attack by the cathode/solvent because the corrosion products include an insoluble salt which forms a thin film on the anode. The salt film, being ionically but not appreciably electronically conductive, behaves as a second electrolyte or "solid electrolyte interphase" in series with the liquid electrolyte and permits electrochemical discharge.

The three systems which have thus far actually appeared as commercial products are lithium/sulfur dioxide, lithium/thionyl chloride, and lithium/sulfuryl chloride. In sulfur dioxide cells, the oxidant typically constitutes
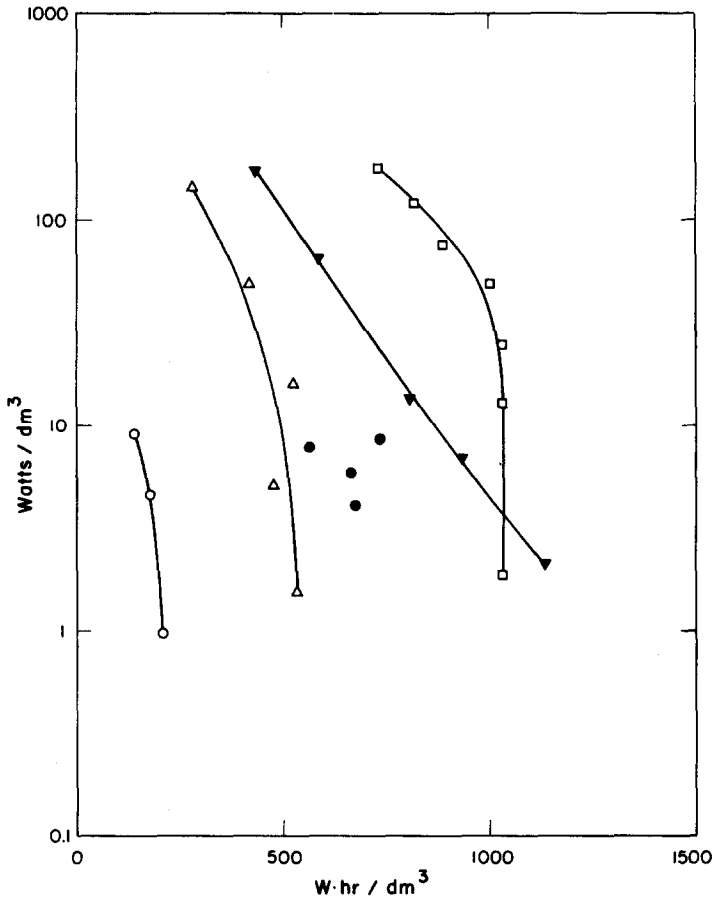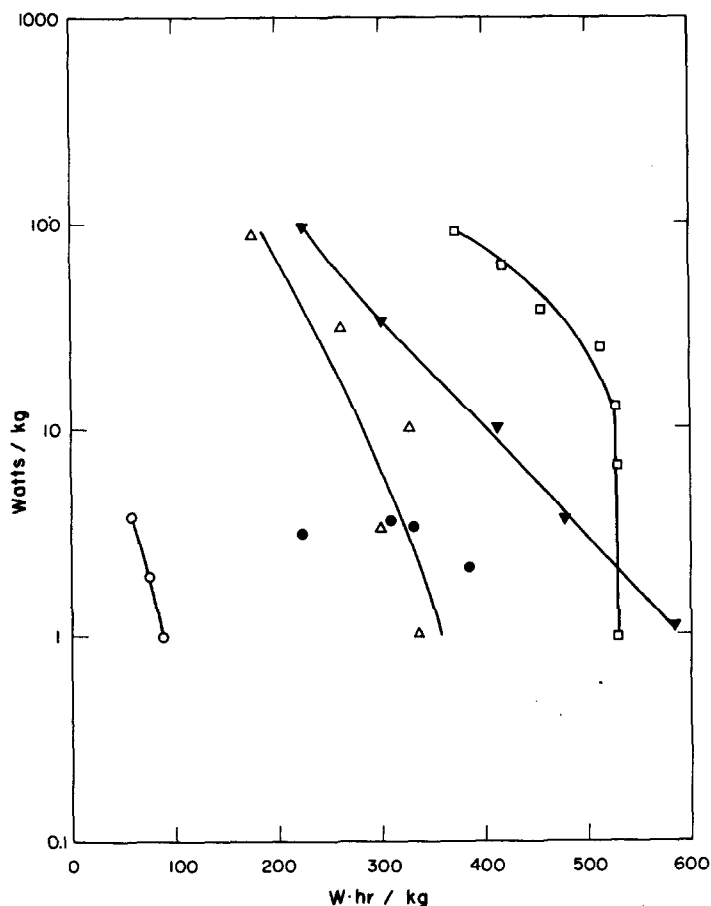

Fig. 1. Volumetric energy *vs.* power density, at normal temperature, for 5 systems. ○, Zn/MnO$_2$ [1]; △, Li/SO$_2$ wound D cells [1]; ●, Li/SOCl$_2$ bobbin cells, sizes 1/2 AA, AA, C and D [3]; ▼, Li/SOCl$_2$ wound D cells [2]; □, wound Li/SO$_2$Cl$_2$ D cells also containing 0.5M Cl$_2$ [4].

Fig. 2. Gravimetric energy *vs.* power density, at normal temperature, for 5 systems. $\circ$, Zn/MnO$_2$ [1]; $\triangle$, Li/SO$_2$ wound D cells [1]; $\bullet$, Li/SOCl$_2$ bobbin cells, sizes 1/2 AA, AA, C, and D [3]; $\blacktriangledown$, Li/SOCl$_2$ wound D cells [2]; $\square$, wound Li/SO$_2$Cl$_2$ D cells also containing 0.5M Cl$_2$ [4].

70 - 80% of the electrolyte, and the cells, as a result, are under about 4 atm of pressure at normal temperature. Cells are made cylindrical to accommo-date pressure, and have been sold in sizes only up to D and DD. Thionyl chloride cells have been sold in sizes ranging from button and wafer cells to 10 000 A h prismatics for reserve power at underground military installa-tions. The initial electrolyte vapor pressure in both thionyl chloride and sulfuryl chloride cells is less than one atmosphere at normal temperature. Sulfuryl chloride cells have been made in sizes ranging from AA to D.

A summary and comparison of the volumetric energy and power den-sities for zinc/alkaline and the three lithium systems at normal temperature are shown in Fig. 1. The same comparison for gravimetric densities is shown in Fig. 2. Each Figure compares alkaline manganese D cells [1] with wound Li/SO$_2$ D cells [1], wound moderate rate Li/SOCl$_2$ D cells [2], four sizes of

Li/SOCl$_2$ bobbin cells [3], and wound Li/SO$_2$Cl$_2$ D cells containing also 0.3M chlorine [4]. The data are representative of devices in which some effort has been made to maximize the energy density in a practical configuration. The energy densities are affected by the current density and the volume and weight of hardware, as well as by the cell chemistry. The bobbin or concentric configuration minimizes the amount of electrode substrate and separator needed, but limits the current capability by limiting the electrode area.

Li/SO$_2$ cells

The lithium/sulfur dioxide cell was the first liquid cathode cell discovered and the first nonaqueous, normal temperature cell which could be discharged efficiently at rates comparable with similarly sized aqueous primary C and D cells. Maricle and Mohns [5] viewed the electrolyte first as a solution of lithium bromide in acetonitrile, which became more conductive as sulfur dioxide was added. Practical cells now contain 70 - 80% SO$_2$, the acetonitrile being necessary to promote the solubility of the lithium bromide [5, 6]. Acetonitrile, which normally reacts with lithium, does not react rapidly as long as sulfur dioxide is present to produce a lithium dithionite solid electrolyte interphase. Propylene carbonate has been used to moderate lithium corrosion when the sulfur dioxide concentration is low [6].

The shelf life and reliability of Li/SO$_2$ cells has resulted in their being recommended for use on the Galileo probe, which demands high reliability after storage for 5 years [7]. The charge retention of DD cells on storage at 25 °C is shown in Fig. 3 [8]. While possible chemical reactions leading to degradation have been discussed, substantial improvements in the choice of hardware has greatly increased stability [9]. Increased stability in electrolyte stored apart from lithium in reserve cells was said to result from the substitution of LiAsF$_6$ for LiBr [10], preventing the oxidation of bromide to bromine [9]. Lithium perchlorate was reported to improve rate capability [11].

The performance of Li/SO$_2$, CH$_3$CN, LiBr cells at reduced temperature is shown in Fig. 4 [12], and can be compared with that for Li/SOCl$_2$ cells shown in Fig. 5 [13]. The Li/SO$_2$ cells were wound CC size with a volume of about 45 cm^3 [12], while the Li/SOCl$_2$ cells were wound D cells, their volume about 51 cm^3 [13]. Each type is shown at 0.5 A, with capacity plotted against potential. The two cell types are roughly equivalent in the way their capacities are limited by discharge at low temperature, except that Li/SO$_2$ cells do not experience as much voltage delay or reduced potential at the onset of discharge following storage. While the higher pressure associated with Li/SO$_2$ cells prevents their use at elevated temperature, Li/SOCl$_2$ cells will function at 150 °C, [56], and with special design, even past the melting point of lithium [57].
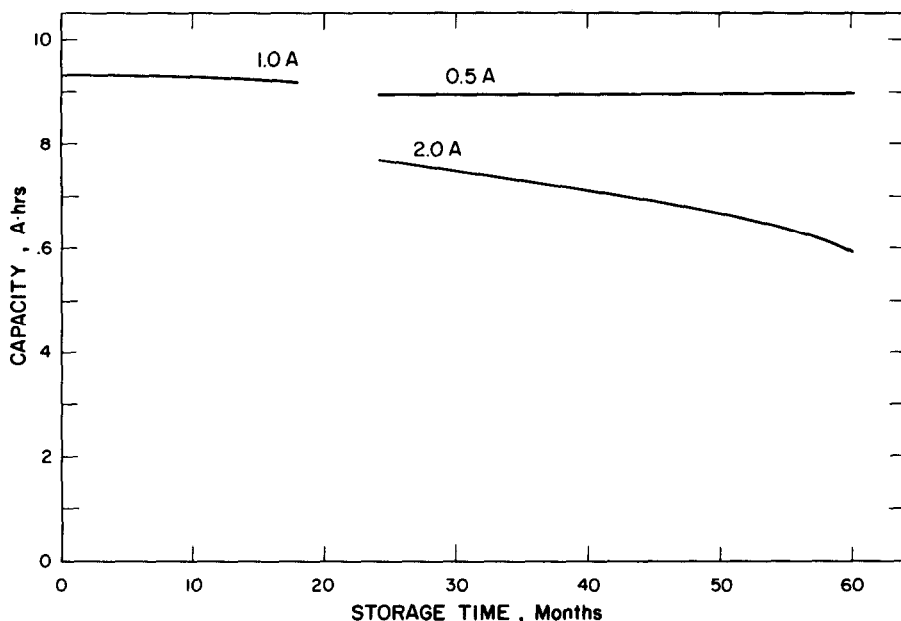
Fig. 3. Capacity retention in NASA Li/SO$_2$ DD cells [8]. Storage and discharge at 25 °C.
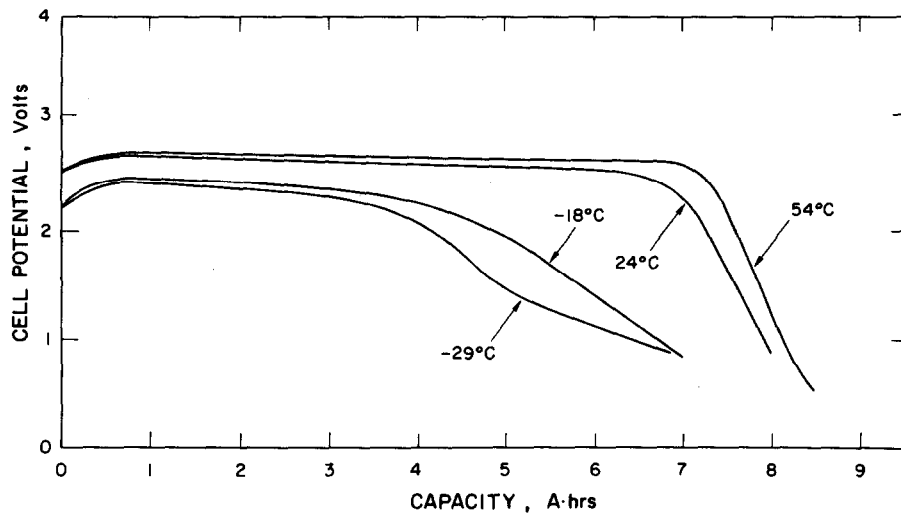

Fig. 4. Discharge profiles (potential *vs.* capacity) for Honeywell Li/SO$_2$ wound CC cells at 0.5 A as a function of temperature [12].

The tendency of Li/SO$_2$ cells on rare occasions to undergo rapid chemical reactions during mechanical or electrochemical abuse, or intermittent storage and discharge, has been of interest since 1975. Reserve cells, containing LiAsF$_6$ and discharged at reduced temperature, were found to be shock sensitive [14]. Taylor and Bowden [15] showed that during overdischarge of
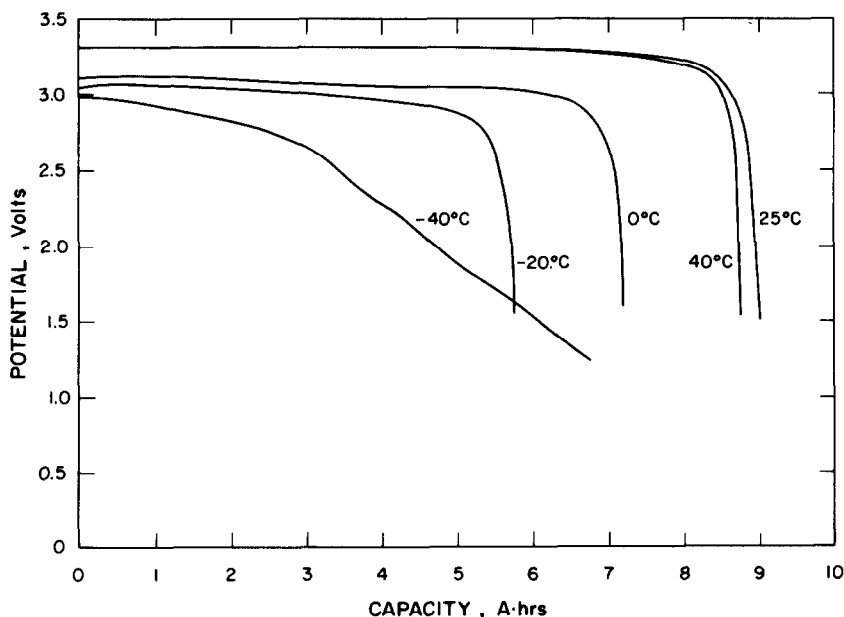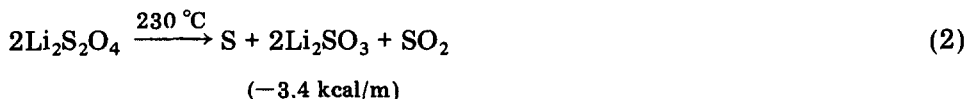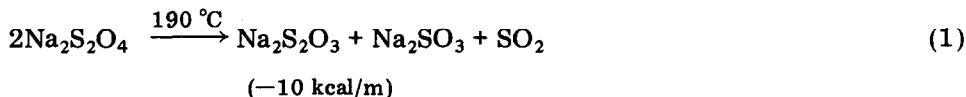
Fig. 5. Discharge profiles (potential *vs.* capacity) for GTE Li/SOCl$_2$ wound D cells at 0.5 A as a function of temperature [13].

carbon limited cells, lithium/aluminium alloy was produced by reduction of lithium on the cathode screen. Methane and cyanide were both recovered from such cells. A possible initiating step for thermal runaway could therefore have been a reaction between Li/Al and acetonitrile. Salts which do not require organic cosolvents to form conductive solutions in liquid SO$_2$ include the lithium salts of halogenated closoborate anions [17], but these materials are more expensive. The thermal decomposition of lithium dithionite, once assumed to be similar to sodium dithionite, was suspected as being an initiator of thermal runaway. However, Oglesby *et al.* have observed the following differences [16]:

$$2Na_2S_2O_4 \xrightarrow{190\ ^{\circ}C} Na_2S_2O_3 + Na_2SO_3 + SO_2 \tag{1}$$

$$(-10\ \text{kcal/m})$$

$$2Li_2S_2O_4 \xrightarrow{230\ ^{\circ}C} S + 2Li_2SO_3 + SO_2 \tag{2}$$

$$(-3.4\ \text{kcal/m})$$

More recently, the discharge of Li/SO$_2$ cells at elevated temperature has been found to produce not just dithionite, as at normal temperature, but sulfur, lithium dithionate, and lithium pyrosulfite as well. A reduction in the available capacity resulted. To change the course of the overall reaction, spirally wound D cells had to be discharged at 72 °C at 3 - 5 A [18]. The heating of discharged cells failed to produce dithionate or pyrosulfite. The

behavior suggested that the reduction of SO_2 proceeded through intermediate species which could react with sulfur dioxide making it unavailable for electrochemical reduction. Using electron spin resonance spectra, Anantaraman *et al.* [19] concluded that in acetonitrile in the presence of tetramethylammonium bromide, sulfur dioxide was reduced to SO_2^-, which reacted reversibly with sulfur dioxide to form $S_3O_6^-$ which, in turn, could react with SO_2^- to form $S_4O_8^{2-}$.

Li/SOCl$_2$ cells

One of the most important differences between Li/SO$_2$ and Li/SOCl$_2$ cells is that the latter are more subject to voltage delay. The most significant cause of voltage delay in Li/SOCl$_2$ cells is the presence of hydrolysis products and iron, which contribute to excessive growth of the lithium chloride solid electrolyte interphase either by lithium corrosion or by increasing the electronic conductivity of the salt film [20]. Hydrolysis products, iron, and excess aluminum chloride can be removed from electrolyte by refluxing with lithium [21]. Passivation can be reduced further by lowering the salt concentration [22], but voltage delay is most significant at higher rates where good electrolyte conductivity is important. Alternative electrolyte salts, such as halogenated closoborates [23], oxyacid complex aluminate salts [24], SO$_2$/AlCl$_3$ complex electrolytes [25], and LiAlCl$_2$S [26] have been suggested.

The overall cell discharge reaction is as follows [21, 27]:

$$4Li + 2SOCl_2 \longrightarrow S + SO_2 + 4LiCl \qquad (3)$$

The discharge proceeds through a series of unstable and metastable intermediates, as evidenced by the thermal behavior of discharged electrolyte [21], the rate of appearance of SO$_2$ in discharged electrolyte [21], the rate of volume change during discharge [28], by the cyclic voltammetric analysis of a solution undergoing controlled potential electrolysis [29], and by ESR analysis [30, 42]. From their cyclic voltammetric analysis, Bowden and Dey [29] concluded that the most likely pathway was first to the diradical SO, then to reversible equilibria with complexes containing thionyl chloride or more SO, followed by irreversible decomposition to sulfur and sulfur dioxide. From the results of ESR studies, discharged electrolyte was believed to contain the radical OClS which, because of its instability, could not be detected unless immediately frozen [42]. The solution was said also to contain radical sulfur species.
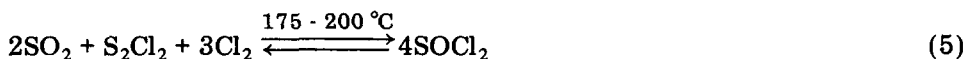
Attempts to obtain reliable and reproducible open circuit potential measurements showed that the results were dependent upon the procedure. In one method, potentials were obtained by fitting curves to linear plots of current *versus* potential and extrapolation to zero current between 72 °C and −60 °C [21]. In another method, a high impedance voltmeter was left across the terminals of a cell at a given temperature until the potential remained constant [31]. In each case, cells had been partially discharged at low rate in an effort to remove any impurities initially present. The potentials found

using the second method were all higher, and showed a negative linear dependency on temperature as opposed to a positive one. Both measurements have since been repeated and confirmed by Klinedinst [32], although several other reports, in which only the static technique was used, have been written.

The entropy change for a reversible cell reaction should be available from either the dependency of the open circuit potential upon temperature, or the heat released or absorbed when the cell is operating under essentially reversible conditions. Gibbard found that the heat released on low rate discharge compared closely with the heat absorbed on charging, correcting for resistive and chemical losses [31]. The calculated entropy (about -12.2 to -14.5 cal $\deg^{-1}$ equiv^{-1}) also compared reasonably well with that calculated from the static open circuit potential $vs.$ temperature measurements (-11 to -18 cal $\deg^{-1}$ equiv^{-1}). The question was therefore raised whether the dynamic technique is a valid method for determining the open circuit potential of the Li/SOCl$_2$ cell.

The determination of entropy change by measuring heat exchange during electrochemical cell reactions depends upon those reactions being reversible ones. The fact that the reaction occurring during Gibbard's low rate charge and discharge tests was reversible is dramatically demonstrated by noting that cells absorbed heat at the same rate when charged at a given current as they had released it when discharged at that same current. Cyclic voltammetric and ESR analyses have indicated that the primary discharge product during the reduction of thionyl chloride decomposes rapidly, particularly in the presence of thionyl chloride itself [29, 42], and the reduction is thus an irreversible one. The reversible reactions occurring during the low rate charge and discharge tests therefore did not represent the reduction of thionyl chloride or the reoxidation of a discharge product to thionyl chloride.

Thionyl chloride can be prepared by heating a mixture of SO$_2$, sulfur, and chlorine [33]:

$$2S + Cl_2 \longrightarrow S_2Cl_2 \tag{4}$$

$$2SO_2 + S_2Cl_2 + 3Cl_2 \underset{\longleftarrow}{\overset{175 \text{ - } 200\,°C}{\rightleftharpoons}} 4SOCl_2 \tag{5}$$

Reaction (5) is reversible, and so small concentrations of chlorine can be expected to be present even in the most carefully purified solvent [34]. The standard entropy change for reaction (6), with chlorine in the liquid state at 25 °C, was estimated to be about -10.2 cal $\deg^{-1}$ equiv^{-1} [35].

$$Li_{(s)} + 1/2Cl_{2(l)} \longrightarrow LiCl_{(s)} \tag{6}$$

The entropy of chlorine adsorbed on carbon, although also in a condensed phase, would likely be higher than liquid chlorine, making ΔS^0 for its reduction by lithium slightly more negative than -10.2. The noted thermoelectrochemical behavior of Li/SOCl$_2$ cells could therefore be conceivably explained by the adsorption of chlorine on the carbon electrode, followed by

its reversible reduction/oxidation. In any case, the careful analyses by Gibbard [31], and by Patel *et al.* [36] are examples which show that Li/SOCl$_2$ cells release heat at all discharge rates. At very low rates, lithium corrosion, decomposition of the primary discharge species, and discharge of adsorbed chlorine apparently all contribute to the released heat.

Lithium/thionyl chloride cells, like Li/SO$_2$ cells, also have a tendency to undergo rapid chemical reactions, particularly when overheated during discharge. The reaction is widely believed to result from the melting of lithium which disturbs the integrity of the protective salt film and allows the electrolyte to reach the metal. Rapid reactions can also be initiated at normal temperature, apparently as the result of local "hot spots" [22] caused by electric sparks or reactions involving impurities and discharge products [37].

Abuse testing of cells has been carried out to determine the causes of rapid reactions induced at normal temperature. Anode limited cells can, for example, be overdischarged without incident as long as the cell design does not permit lithium to become detached from its substrate before it is completely discharged [38]. The oxidation of the electrolyte on the bare anode substrate during overdischarge has led to the formation of Cl$_2$, AlCl$_3$, SO$_2$Cl$_2$, SCl$_2$, S$_2$Cl$_2$, and unidentified materials absorbing in the infrared at 690 and 1070 cm^{-1} [38 - 40]. Salmon *et al.* assigned the 1070 cm^{-1} absorption to SO^{2+} and the 690 cm^{-1} absorption to the explosive Cl$_2$O, by comparison with a spectrum of LiAlCl$_4$/SOCl$_2$ to which Cl$_2$O had purposely been added [39]. No other corroborative evidence such as chemical or other spectral analysis was given. Strong, sharp absorptions at 1070 and 690 cm^{-1} can also be produced by refluxing SOCl$_2$ containing 1.8M LiAlCl$_4$ with solid, anhydrous Li$_2$SO$_4$ for several days [41]. Analysis showed that electrolyte-soluble species produced sulfate when aliquots of the electrolyte were hydrolized. It is unlikely that refluxing with Li$_2$SO$_4$ would have been capable of producing either SO^{2+} or Cl$_2$O in SOCl$_2$/LiAlCl$_4$. Lithium–sulfur oxyacid salts were found in small amounts in cells opened after discharge [21], and so such materials are available in discharged cells to take part in producing these species. A more likely cause of rapid reaction induced at normal temperature is thought to be initiated by Li$_3$N on Li in the presence of HCl [37].

Lithium/thionyl chloride cells with catalyzed cathodes, yielding higher capacity and running potential at higher rate or current density, have contained copper salts [43], metal phthalocyanines [44], platinum [45], or, most recently, the metal complex tetraazaannulenes [46]. In at least one case, the catalyst was claimed to cause improvement by altering the discharge reaction [46].

Li/SO$_2$Cl$_2$

During discharge, the sulfuryl chloride cell produces twice as much SO$_2$ per equivalent of charge as does the thionyl chloride cell, but no sulfur [47].

$$2Li + SO_2Cl_2 \longrightarrow SO_2 + 2LiCl \tag{7}$$

Lithium corrosion is greater in sulfuryl chloride than in thionyl chloride [48], but both corrosion and voltage delay can be essentially eliminated by adding 25% $SOCl_2$ or 7.5% SO_2 and replacing $LiAlCl_4$ with 0.25M $Li_2B_{10}Cl_{10}$ [49].

The carbon electrode in sulfuryl chloride is also profoundly affected by the presence of platinum. At 10% Pt, Shawinigan black cathodes showed nearly 15 times the current density at 3 volts *vs.* Li than uncatalyzed cathodes at normal temperature [49].

Calcium/thionyl chloride and calcium/sulfuryl chloride cells

The theoretical volumetric and gravimetric energy densities of cells using calcium are close to those calculated for lithium when each is considered against thionyl or sulfuryl chloride. The attractions which calcium holds are its higher melting point (842 °C as opposed to 178 °C for Li) and its reduced tendency to form dendrites during cathode limited cell reversal [50]. Correcting for polarization losses, Meitav and Peled [50] estimated that the energy density of a calcium/thionyl chloride cell would be about the same as a lithium/sulfur dioxide cell. Both the difficulty in plating calcium on a metal substrate and the overpotential for anodic discharge are believed to be the result of anionic rather than cationic conduction in the solid electrolyte interphase. Cathodes polarize more easily in $Ca(AlCl_4)_2/SO_2Cl_2$ than in $LiAlCl_4/SO_2Cl_2$ [51], and in $Ca(AlCl_4)_2/SOCl_2$ than in $LiAlCl_4/SOCl_2$ [52], evidently because the solution transport of calcium is slower.

The corrosion of calcium is unacceptably high for practical cells. Staniewicz found that precoating calcium with calcium oxide [52] improved the stability somewhat, but still, 20% of the calcium was lost through corrosion and 40% trapped within a salt matrix and electrochemically unavailable. The anodes were originally about 0.020 in. thick, and discharged at 0.5 mA/cm^2 at normal temperature. Gupta and Fritz [54] attempted to limit the corrosion by alloying calcium with lithium. About 9% of lithium was necessary to stop anode polarization on discharge at 0 - 10 mA cm^{-2}. Calcium/10% lithium has a melting point of about 800 °C.

Other liquid cathodes

In an effort to attain increased safety without significant sacrifice of performance or energy density, other liquids have been investigated as cathode materials *vs.* lithium. In a survey of halogenated organic solvents, Smith *et al.* [53] found that $LiAsF_6$/50% $CClF_2$–CH_2Cl plus 50% tetrahydrofuran discharged on carbon at about 1.5 volts *vs.* Li, showing capacities of about 2A h/gram of carbon. Dimethylsulfoamoyl chloride ran at about 2.8 volts, but showed a lower capacity per gram of carbon.

Chlorine [4], bromine, and bromine chloride have all been considered as additives to Li/SO_2Cl_2 cells, and iodine chloride by itself has also been considered as a liquid cathode material [55].

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