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A REVIEW OF CELLS BASED ON LITHIUM NEGATIVE ELECTRODES (ANODES)

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Contents

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Summary

This review traces the development of lithium cells from their inception to the present day: about 500 references are included. Primary and secondary cells are dealt with and the most useful anode/cathode combinations, in both fields, are noted. Electrolytes and separators are also discussed, as are the effects of film formation and the charge/discharge mechanisms.

Shortcomings are emphasised where they are known to exist and attention is drawn to some areas where the present authors consider advances may be made.

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1. General introduction

The need for high energy density batteries which can be used both at high and at low discharge rates, and under stress conditions, has led to the use of active metals as battery anodes. In particular, cells using lithium anodes and various types of cathodes have been developed because of their high equivalent weights and free energies. The performance of some of these couples is discussed and the discharge processes which are involved are reviewed.

There has been rapid development of primary and secondary lithium batteries during the past decade and a considerable number of cathode materials have been used to try to obtain a high energy system. New electrolytes or separators have also been developed because the cathode materials may dissolve in the electrolyte.

In many cases the theoretical and practical energy densities and working voltages do not correspond. To explain this, new discharge processes have been proposed and in some cases verified.

In this paper, we examine the battery in terms of its cell components, and discuss the role of film formation and discharge mechanism on the cell performance. We list the properties of a large number of types of cell, but make no attempt to pull together the general area of lithium cells.

The use of water as a solvent seriously limits the potential energy density of cells due to its reactivity with respect to the components of the more thermodynamically interesting electrochemical pairs. Conventional systems have poor shelf lives due to hydrogen evolution, and low energy densities due to the low thermodynamic decomposition potential (1.23 V) of the solvent (water) which results in lower cell voltages. The energy densities of some common cell types are shown in the Table.

Cell	W h/kg	
	Theory	Practice
MnO_2/Zn	400	90
HgO/Zn	260	150
NiOH/Cd	240	130
Pb/PbO_2	250	130

If the water could be replaced, then numerous other couples possessing considerable theoretical energy densities could be developed, for example: Li/F which has a theoretical energy density of 6250 W h/kg [1].

Theoretical data [1] suggested that lithium would be the best anode, but until recently it could not be used.

Li	Na	Be	K	Mg	Sr	Al	
12	2.5	11	2	5.5	1.5	5.0	W h/kg

Interest in the use of lithium as the anode in high energy batteries was only rekindled when it was shown [2] that metallic lithium could be deposited from organic electrolytes comprising lithium salts dissolved in organic solvents such as propylene carbonate (PC). γ-Butyrolactone (BL) and PC were found to dissolve a variety of lithium salts and to become a reasonable conducting medium in which the lithium was stable. This has led to the rapid development of lithium primary batteries which can have high working voltages, high energy densities, and long shelf lives.

Experience with these organic electrolytes has, however, limited the choice of the anode to lithium. This is because sodium and potassium depositions from non-aqueous solvents are accompanied by solvent reduction [3], and magnesium [4] and aluminium [5, 6] are only deposited from free metal alkyls containing electrolytes which are not suitable for batteries.

2. Primary cells

2.1. *Introduction*

During the last decade lithium primary cells have become established as relatively cheap, reliable power sources. The cells which have been commercially exploited successfully are those based on the solid cathodes CuO, $C(F_x)_n$ and V_2O_5 materials, together with the liquid/gaseous sulphur dioxide and thionyl chloride systems.

A large number of other combinations are possible and we attempt in this review to consider the totality of the electrodes and the various electrolytes used in the primary cells containing lithium anodes.

2.2. *The lithium anode*

Although lithium is mechanically strong, has a low equivalent weight (6.9), a low density (0.53 g/cm^3 at 0 °C), and a high equilibrium potential [7], there are numerous difficulties in overcoming the considerable losses due to polarization of the electrodes. A number of electrode configurations [8] have been considered in the development of these cells, but the best performance seems to be achieved by plating the lithium directly onto a metallic conductor — nickel or aluminium. Recently, more attention has been given to Li/Al alloys because of their possible use in lithium secondary cells and because of their good cycling properties.

2.2.1. *Kinetics of lithium electrodes*

The kinetics of lithium electrodes in numerous organic electrolytes have been studied [9 - 14]. In particular, investigation of the transport phenomena of lithium cations in organic solvents [15 - 17] show that the transport number (t^+) of the lithium cation (Li^+) is 0.4, and the diffusion coefficients are about 10^{-6} cm^2 s^{-1}.

2.2.2. *Stability of lithium in specific electrolytes*

(a) Dimethyl sulphoxide (DMSO). Lithium was found to be strongly attacked within two hours by a solution of DMSO containing $CuCl_2$. A $LiClO_4$/DMSO solution, however, took much longer [18] and pure DMSO, LiCl, LiF, CuF_2 showed only slight, if any, attack on lithium after 168 h [19]. The rate of gas evolution in the Li/$LiClO_4$, DMSO system at 30 °C was also shown to be negligible [20].

These varied reports indicate that impurities, acids or water, which are introduced into the cell along with the solutes, must be removed for good cell performance [21].

(b) Propylene carbonate (PC). Lithium is relatively stable in pure PC [22 - 25] and in $LiClO_4$–PC solutions [26 - 28] and is very stable in $LiBF_4$–PC [29]. Solvent degradation occurs in the presence of $AlCl_3$, however, and this results in the formation of CO_2 and chlorohydrins, which leads to a high

corrosion rate accompanied by hydrogen evolution [30, 31]. Lithium corrosion in $LiAlCl_4$/PC has been mentioned by Jasinski [32, 33]; the reaction products were identified as carbon dioxide, water, hydrochloric acid, propylene oxide, allyl alcohol, n-propyl alcohol, propylene glycol and propionaldehyde [34]. It was thought that the strong Lewis acid generated in the dissolution equilibria of the $AlCl_4^-$ anion was primarily responsible for the formation of these products [34]. Because of the possible development of secondary cells, more attention has been paid to the solvent. In particular, numerous experiments have been carried out on Li and Li/Al alloys in PC [381]. Cycling of Li in PC results in the formation of passivating anodic layers on the Li at free ohmic resistances above a critical value. This causes dendritic deterioration and thus a decrease in the cycling efficiency [382], which may be restored by the addition of Al salts [381].

(c) Water. The discharge of the anode is minimally affected by low concentrations of water (50 - 200 ppm) [35 - 38], whilst higher concentrations form passivating films of LiOH [37, 38]. The specific effect of water on the discharge of lithium has been studied using potassium thiocyanate (KSCN) in PC [39]. A negligible change in the anode potential was observed even when the water in the anode compartment rose to 5%.

2.3. Cathode materials

Although the development of liquid and gaseous depolarizers for primary lithium batteries is well advanced, it has not hindered the development of solid cathode materials for high energy, low rate applications. This is not only because of their parity with those systems at low rates of discharge but also because of their advantages of safety, corrosion resistance, and ease of handling.

The main requirements of cathodic materials have been discussed [40] and include:

(i) a low equivalent weight;
(ii) a high potential *versus* the anode;
(iii) stability in the electrolyte;
(iv) electrochemical activity;
(v) low solubility in the electrolyte;
(vi) a good conductivity.

The cathode may dissociate [41]:

$$CuS \rightleftharpoons Cu^{2+} + S^{2-}$$

or it may be involved in complex formation:

$$CuCl + Li^+ + e^- \rightleftharpoons Cu + Li^+ + Cl^-$$

$$CuCl + Cl^- \rightleftharpoons CuCl_2^-$$

The discharge behaviour of the cathode depends on whether it is a conductor, a semi-conductor or an insulator. Conductors are usually insoluble in the electrolyte and have a high discharge rate. Semiconductors need additional conducting material such as graphite [42], acetylene or carbon black, or nickel or silver powders [43] to achieve a reasonable current density. As graphite is not inert [45] tungsten carbide and boron nitrides have been used instead using PVC or PTFE binders [42]. Insulators are rather soluble materials but can give good current densities although they do induce a rapid self-discharge rate.

The main group of cathode materials which has been proposed, or are in use, are:

(i) halogens and halides;
(ii) chalcogens and chalcogenides;
(iii) metal oxides;
(iv) sulphides and selenides;
(v) oxysalts;
(vi) organics;
(vii) $(CF_x)_n$;
(viii) SO_2.

2.3.1. Halogens

The halogens are active oxidants and have high theoretical energy densities, but the problems in handling gaseous depolarizers are formidable.

(a) Fluorine. As yet fluorine may not be used in lithium cells, but ClF_3 has been tested and its reduction properties investigated by cyclic voltammetry [46].

(b) Bromine. The cell Li/0.2M LiBr, PC has been developed [47] but the use of bromine as a depolarizer is limited because of its solubility in organic solvents. Attempts to develop a polyethylene separator which prevents the diffusion of Br_3^- to the anode compartment have met with limited success [48]. Recently [366] more successful cells have been developed by increasing the conductivity of Br_2 in the organic solvent. The high ohmic resistance of the discharge product, however, remains a serious problem.

(c) Iodine. As soon as lithium is brought into contact with iodine a film of LiI, which is a poor conductor, is formed [49 - 53]. To increase its conductivity iodine cathodes containing 50% of polymeric 2-vinylpyridine have been used. In the case of the Li/I_2–polyvinylpyridine (PVP) cell, the internal resistance of the cell was reduced and the current capacity increased by precoating the Li anode with PVP [367].

2.3.2. Halides

Transition metal fluorides may be used and, because of the stability of LiF (ΔG formation = −139 kcal), a high cell potential results. The cells which have received most attention are the halides of Cu, Ag, and Ni. On discharge a volume reduction is expected which would result in additional pore formation within the electrode structure [54]; for example, NiF_2 (density 4.6 g/cm^3) on discharge produces Ni (density 8.9 g/cm^3). This would be an advantage in the discharge of primary cells.

Many such materials are insulators, but, as the discharge products are often conductors, conductive filaments build up through the electrode and there is no need to add a conductive diluent.

(a) Copper fluoride (CuF_2). Given the equivalent weights and free energies of active materials, the energy density of the Li/CuF_2 cell (749 W h/lb) is three times that of the Zn/AgO cell (254 W h/lb) [55] and a method for the construction of such a cell has been patented [56]. Electrodes without polyethylene binders are characterised by poor performances, and the use of acrylic binders has been reported to decompose the CuF_2 [57]. The electrolytes used are either $LiClO_4$ in PC or $NaPF_6$ in a mixture of PC and BL. If the concentration of $LiClO_4$ is decreased, the cell's capacity decreases. This can be related to the proportionality between CuF_2 solubility and the $LiClO_4$ concentration due to the metathetical reaction:

$$CuF_{2(s)} + 2LiClO_{4(sol)} \longrightarrow 2LiF_{(s)} + Cu(ClO_4)_{2(sol)} \quad [59]$$

Discharge efficiencies are as high as 85% in $LiClO_4$ to a cut-off voltage of 2 V with a current density of 0.03 mA cm^{-2}.

CuF_2 is slightly soluble in DMSO [60] but this need not inhibit its use as a cathode, provided it does not plate out at the anode discharging lithium.

(b) Copper chloride ($CuCl_2$). This material is quite soluble in PC and dimethylformamide (DMF) [61, 62]. Attempts to minimise its solubility by the common ion effect, using mixed solvents and complexing anions, have not been effective and, because of this, the system Li/LiCl, DMF/$CuCl_2$ is used as a reserve battery.

(c) Copper iodide (CuI). In an attempt to develop a secondary battery, copper iodide has been used. The system developed contains either CuI or PbI as the cathode, which is interspersed with 30% Cu or Pb powder and contains a modified LiI electrolyte. The discharge product of these cells is LiI. A drawback of such cells is that their capacity decreases on cycling [368], and at present they can only be used for low rate applications.

(d) Nickel chloride ($NiCl_2$). This is insoluble in the LiCl, $AlCl_3$, PC system and its construction has been described [63, 64]. Nickel chloride reacts with the electrolyte resulting in a chloride deficiency within the electrolyte. This may be one reason for the cell's poor discharge characteristics although they have been improved by treating the electrolyte with Cl_2 [65].

(e) Silver chloride (AgCl). A cell of the type Li/$AlCl_3$, PC/AgCl [66] has been described and is constructed by using the wet paste technique [67].

(f) Mercury fluoride (HgF_2). The material in the system:
Li/PC, phenyltrimethyl ammonium/HgF_2, acetylene black, Ag hexafluorophosphate has a theoretical energy density of 343 W h/lb with an open circuit voltage of 3.6 V [83]. The acetylene black is present as a conductive diluent, and the Ag is present to prevent amalgamation with the Hg.

In practice, the cell only delivered 41% of its capacity at an average voltage of 1.6 V at a discharge rate of *C*6 or less. Self-discharge was also considerable over a period of two weeks.

(g) Cadmium fluoride (CdF_2). This material is an insulator with an energy gap of 6 eV. By doping it with Y(III), however it becomes a semiconductor with a resistivity of 1 Ω/cm [84, 85]. The energy density of the cell (399 W h/lb) [86, 87], coupled with the improved discharge voltage of the doped material (2.4 - 2.6 V compared with 1.7 V for the normal material), makes this an attractive cell for many applications.

(h) Bismuth fluoride (BiF_3). This material is a non-conductor so that graphite, acetylene black, Ag or Bi must be added as conductive diluents. Numerous electrolyte combinations may be used without detriment to the cell's energy or capacity. They include $LiPF_6$–tetrahydrofuran (THF), $LiClO_4$–THF, $LiPF_6$–BL and $LiClO_4$–PC. The material is slightly soluble in $LiPF_6$–PC which results in a lower shelf life. Unlike other fluorides (CuF_2, AgF_2 and NiF_2), BiF_3 is fairly insoluble in $LiClO_4$ containing electrolytes and therefore it has a longer life in this system. It has a theoretical capacity of 0.302 A h/g and an open circuit voltage of 2 V [88].

The main advantage of this cell is that it has low polarization losses at current densities above 1 mA/cm^2, but its major disadvantage lies in its poor voltage regulation.

(i) The use of 'crown ethers'. The use of crown ethers [68, 69] which can dissolve fluorides has led to the development of new high energy batteries which have high open circuit voltages and a reasonable current delivering capability [70]. An example of such a cell is:

Li/LiF, DC 18C6, solvent/NiF_2

The nature of the solvent in this system has not been disclosed by the manufacturers.

Silver and copper halides may be discharged at high current densities but, as they form soluble complexes which lead to high discharge rates, their practical use is limited, and the high current densities are only achieved because of the considerable solubility of these materials *via* complex formation [71 - 74]. For example:

$CuCl_2 \longrightarrow CuCl_2^-$ and $CuCl_4^{2-}$ [75]

$AgI \longrightarrow AgI_2^-$ and $AgI_x^{(x-1)}$ [76, 77]

Because of their solubility, self-discharge and dendrite formation are serious problems [78], limiting their storage life to less than one month.

Nickel fluoride, CuF_2 and HgF_2 form insoluble complexes but show a much poorer discharge mechanism which indicates the importance of solubility in the discharge of the silver and copper halides, despite the disadvantage it brings.

To overcome the formation of soluble complexes ion-exchange membranes were used [79 - 81], but they had a higher specific resistance than the electrolyte — 10^3 Ω cm^{-1}. This resistance was decreased by using thinner membranes which had a higher capacity [82], but the results were not successful.

2.3.3. Chalcogens

(a) Sulphur. The lithium/sulphur system has attracted much attention [89 - 97]. The formation of S_8^- and of polysulphide species [98 - 100] leads to a considerable loss of cathode material and to corrosion of the anode by the reaction:

$$2x\mathrm{Li} + \mathrm{S}x^2 \longrightarrow (x-1)\mathrm{Li_2S} + \mathrm{S}^{2-} + 2\mathrm{Li}$$

The addition of BF_3 to the electrolyte increases the efficiency by reducing the formation of the polysulphides as a result of the formation of an adduct between the sulphide and the BF_3.

Recently a prototype Li/S cell has been developed:

Li/5M S as Li_2S_n in THF and 1 M $LiAsF_6$/C

using a Teflon-bonded carbon current collector. This cell had practically 100% of its theoretical capacity available at 50 °C at rates below 1 mA cm^{-2}, and at 4 mA cm^{-2} 75% of the cathode utilization is possible. At high rates the capacity is enhanced by adding Lewis acids. Using a standard cell design this system has a practical energy density of 300 W h/kg. If an electrolyte additive could be found which dissolved the Li_2S which precipitates in the pores of the cathode, then this cell could be used as a power source for high discharge applications at room temperature.

Some chalcogenides also show promise of practical utilization [102]. They have received more attention recently because of their possible use as special power packs and because they may be used as cathode materials in secondary cells [369]. Their role in the latter has been discussed and the thermodynamics which governs their reversibility at ambient temperature established [370]. At ambient temperature two possible reaction mechanisms are possible, displacement or insertion. The former is irreversible whilst the latter is a function of temperature. Much attention has, therefore, been placed on chalcogenides which undergo insertion reactions [370] without being affected much by temperature.

2.3.4. Metal oxides

Metal oxides are potentially good as cathode materials because they are safe, easy to handle, common, economical, possess high theoretical energy densities, and long life. Copper oxide (CuO) [103], V_2O_5 [104], MoO_3 [103], and Mo_8O_{23} [106] have proved suitable in this sense.

(a) Copper oxide (CuO). This material produces a practical open circuit voltage of 2.4 V whilst that based on the first reduction step, CuO/Cu_2O, is 2.35 V. On load, the voltage drops to between 1 and 1.4 V depending on the discharge rate, but it is completely restored after partial discharge. The capacity is 3.83 A h/g compared with the theoretical capacity of 3.95 A h/g.

There is only a 5% loss in capacity after six months storage. Under conditions of continuous discharge, the Li/CuO system gives a better performance than the alkaline MnO_2 and Leclanché cells when the current drain is less than 55 mA. The Leclanché system gives greater capacity on intermittent discharge due to its capability of recovery.

(b) Vanadium pentoxide (V_2O_5). The development of this cell with its open circuit voltage of between 3.5 and 3.75 V and an energy density between 200 and 220 W h/kg has been described in the literature [107, 111]. The material is a non-conductor, and its discharge products are also non conductive. Because of this, graphite is added as a conductive diluent to the cell which uses $LiClO_4$–THF, $LiClO_4$ in THF and PC, or $LiAsF_6$ in methyl formate (MF) [112] as the electrolyte. Although the cell has a good shelf storage — under 3% loss in capacity after two years — its poor voltage regulation (the discharge characteristic exhibits two or three plateaux) is a serious drawback in its use as a cathode material in primary cells.

(c) Molybdenum oxide (MoO_3). Cells using this material have open circuit voltages of 2.8 V and an energy density of 442 W h/kg. Its use as a cathode was first suggested by Knapp [113]. Since then several authors have investigated this material [114 - 120], but the cathode reaction is not clear. It is thought that it involves a two electron transfer per molecule of MoO_3. Campanella and Pistoia [121] using $LiAlCl_4$ and γ-BL, however, showed that the open circuit voltages were higher than those predicted from thermodynamic data, assuming the products to be Li_2O, MoO_2 or Mo_2O_5. Popov and Laitenen [122] have suggested that the primary reaction products react further with MoO_3 forming polymolybdates.

A large increase in capacity was observed when 1M $LiClO_4$, THF–DME rather than $LiClO_4$, PC was used to prepare the electrolyte and can be attributed to the increased diffusion of $LiClO_4$ in the THF–DME mixture.

Molybdenum oxides with formulae between MoO_2 and MoO_3 are now being considered as cathode materials in secondary lithium cells. Of those considered, $Mo_{17}O_{47}$ in $LiClO_4$/PC seems the best. The OCV of this cell is 1.85 V, and it can supply current densities of 15 mA/cm^2.

(d) Silver oxide (AgO). The system Li/LiBr, DMSO/AgO has been reported to achieve 400 W h/lb of electrode material at a discharge rate of 10 mA cm^{-2} [123] and has an open circuit voltage of 3.43 V.

(e) Titanium dioxide (TiO_2). This oxide has been investigated [124] because of its high theoretical energy density (950 W h/kg). The theoretical open circuit voltage, based on a one electron transfer is 1.1 V, but the practical value is 2.85 V. Anatase-TiO has now been developed as a cathode in secondary lithium cells which can be used at ambient temperatures [376].

Numerous other metal oxides have been used or suggested, but apart from the AgO, CuO systems the rest can only be discharged with low efficiencies and high polarization.

(f) Manganese dioxide (MnO_2). This oxide has been thoroughly investigated in the last few years because of its applicability both at low (0.1 - 5 mA cm^{-2}) and at high (10 and 25 mA cm^{-2}) continuous discharge rates. At such high rates the electrolyte (50% 1M $LiClO_4$/PC: 50% THF) was stable and no gassing occurred. A simple model for the band structure of MnO_2 can be used to explain the open circuit voltage of MnO_2 electrodes as a function of the degree of discharge [373].

A pasted type of MnO_2 has now replaced the powdered material used in earlier cells [374].

2.3.5. Sulphides and selenides

These materials have the advantage of being conductors [125].

(a) Copper sulphide (CuS). This is the most important sulphide and, with an open circuit voltage of 2.15 V, has been widely studied [127 - 132]. One cell uses an electrolyte of 1M $LiClO_4$, 70 parts THF and 30 parts 1,2-dimethoxyethane whilst another uses $LiClO_4$ in THF/isopropylamine (IPA). The sulphide itself does not form complexes but the discharge products [133] in the IPA solvent do form complexes of Li_2S–IPA. By mechanically preventing the swelling and deformation of the electrodes which would occur as a result of this complex formation, the cell performance is increased from 70 to 250 h at a 5 ohm discharge and has an energy density of 300 W h/kg. For applications where multiple voltage plateaux are undesirable, cells can be made with excess cathode material [134] without sacrifice of the energy density of the cell. The voltage of this cell is stable through 90% of its discharge life and in the last 10% of its discharge it again falls to another stable plateau [372].

(b) Potassium iron sulphide ($KFeS_2$) and $M_{0.5}FeS_2$(M = Sr, Ba) [135].

These materials have a high theoretical energy density and an open circuit voltage of around 2 V. They behave as reversible cathode materials which are characterised by Fe being in the +III state, and by having infinite chains of edge-shared tetrahedra supported by the alkali or alkaline earth metals.

Some sulfospinels [375] have been, and are being, extensively studied because of their potential reversibility. The most widely studied are $CuCo_2S_4$, $CuNi_2S_4$, $CuNiFeS_4$, $CuFeS_4$. Reversible cycling in such cathodes is due to interstitial migration of Li into the face centered cubic structure. Of those mentioned, the first and second compounds are best.

(c) Mixed sulphide cathodes. In these systems the cathode consists of a mixture of two sulphides, for example, TiS_2 and MoS_3 [136]. The TiS_2 is mixed with a higher energy density but lower rate cathode material, which allows retention of the latter's high capacity whilst permitting high current pulse discharges. This rate compatability depends on matching the discharge voltage profiles of the two components. Molybdenum trisulphide has a high capacity (1.1 W h/g) whilst the TiS_2 or VSe_2 act as the high rate, low capacity component which enhances the discharge behaviour of MoS_3. This method has also been applied to MoO_3, V_2S_5, V_2O_5 and V_6O_{13} which have high theoretical capacities but poor rate capabilities or conductivities.

Other materials such as TiS_3 and $NbSe_3$ [137] have been used as cathode materials and the borosulphides [126], AgBS, CuBS, have also been suggested because of their high theoretical energy densities (890 W h/kg) although, in practice, it is only 190 W h/kg.

2.3.6. *Aluminium complexes*

It has been found [377, 380] that additions of an Al containing electrolyte to the solvent can minimise dendritic growths and that alloying of the substrate with Li improves the cycling behaviour of the Li. Discharge reactions using Al as substrate allow peak current densities of 10 mA cm^{-2} at ambient temperatures. This has proved suitable for low rate applications in secondary cells [378]. Cells of the type Li/Al/PC–$LiAlCl_4$/graphite [379] have an open circuit voltage of 4.0 V. The $AlCl_4^-$ is oxidised with the formation of Cl_2 which eventually saturates the solution. There is no evidence to suggest that the graphite is oxidised before the PC.

2.3.7. *Oxysalts*

Many oxysalts have been studied [138 - 146]. In the Ag_2CrO_4 system [139], the electrolytes used are either 1M $LiClO_4$ in PC or in a mixture of PC and THF. The THF is used to reduce the viscosity and improve the rate capability of the cell by improving the mass transport in the cathode. The open circuit voltage of this cell is 3.35 V but the performance of this system is poor if based on a two electron transfer. A deeper discharge process, however, has been suggested for these cathodes [147] which increases the capacity obtainable from the cells. The use of graphite-free systems, also noted for other oxysalts [148 - 151], seems to be possible due to a high intrinsic porosity which allows the permeation of the electrolyte.

On the basis of cost, stability, and ease of preparation, the silver and copper tellurates, molybdates, and tungstates have been extensively studied [152, 153]. These cells usually contain $LiAsF_6$–BC as the electrolyte, but have the advantage of being stable in most common electrolytes, with the exception of those containing halides. In certain cases they compare favourably with Ag_2CrO_4. The silver tellurate is the best, and may be discharged at 0.5 mA cm^{-2} or 8 mA cm^{-2} with relatively high cathodic efficiencies. The electronic conductivity is due to metallic silver which is formed as the discharge continues. Bonino and Lazzari (1978) [152] have shown that molybdates are good cathode materials in small-sized lithium cells. The power density from the di- and decamolybdate is about 0.5 W h/g. The discharge mechanism is not known but it involves a two step process, the reduction of silver followed by that of the anion. Polymolybdates seem to have a continuous discharge process, but, again, the mechanism is unknown. Even in the silver chromate cell the exact nature of the discharge process has not been clarified [154].

2.3.8. *Organic cathodes with depolarizers*

Numerous organic positives: aromatic and aliphatic nitro compounds, *N*-halogens and quinone have a high theoretical energy density, and despite their extensive testing [155 - 160], the outlook of developing a high performance cell seems poor. This is because of their high solubility which leads either to rapid self-discharge or to passivation of the lithium electrode. For activated cells this is not a problem as solubility allows high discharge rates: short circuit currents of 200 mA cm^{-2} have been obtained from a stationary Li/dichloroisocyanuric acid cell [161, 162].

Pyromelletic dianhydride [161] (PDA) has also been used. It had an open circuit voltage of 3.6 V which dropped to 3.2 V but remained steady for several weeks. Based on a two electron transfer this cell has a theoretical energy density of 740 W h/kg. Its discharge is improved by adding an insoluble proton donor such as pyromellitic acid to give it a specific capacity of 0.5 A h/g and an energy density of 1300 W h/kg at low discharge rates when the cathodic efficiency tends to 100%.

Results [163] have also shown the possibility of using H_2O, HCOOH, HCHO and CH_3OH as cathodic reactants in organic solutions. The cathode of these materials is the hydrogen electrode whose potential depends on the acidity of the material employed as the proton source and on the catalyst. The current densities obtained from such cathodes can be very high, but were not achieved in the prototypes due to the high internal resistance of the Teflon or PVC separators. With the methanol prototype, hydrogen was liberated in the cathode compartment, but the cell still had an open circuit voltage of 3.1 V, an energy density of 3.2 kW h/kg, and gave 700 h service. Dimethyl sulphite has also been used as an organic cathode and the system $Li/LiClO_4(MeO)_2SO/C$ has been developed. The discharge curve shows a plateau at 5.1 V and two others at 4.2 and 3 V. $(MeO)_2SO$, which is the solvent, is the primary reactant but is degraded at above 4.6 V relative to Li [393].

For secondary lithium cells various phthalocyanines, which have good cycling characteristics, have been developed as cathode materials. On the basis of the weight of the cathode material only, the best system was Li/phthalocyanine iron which has an energy density of 1440 W h/kg. The cycle life of the Li/Cu phthalocyanine system is greater than 150 times at a depth of 157 W h/kg. The reaction in these cells is by intercalation between the phthalocyanine molecules [394, 395].

2.3.9. Oxyhalides

$POCl_3$, SO_2Cl_2, and $SOCl_2$ have all been used [164 - 169] and at present the interest in them is centred on their own catalytic reduction at solid electrodes [170 - 174]. Discharge efficiencies greater than 100% are commonly observed [125 - 177] due to solvent reduction on the discharge of conventional cathode materials such as CuF_2 in oxyhalide electrolytes.

In the case of the Li/sulphuryl chloride (SO_2Cl_2) system, high currents at high voltages can be obtained. The drawback is that, on storage and long term standing, passivation of the anode and deactivation of the cathode occurs [383].

The Li/thionyl chloride($SOCl_2$) cell has been intensively investigated [383a] because of its high rate, high open circuit voltage and high energy densities. It is potentially reversible, although the Li behaves as a reversible electrode of the 2nd order which decreases the working voltage [383]: because of this a large Li electrode is used. The reduction of $SOCl_2$ is very complex. Numerous products have been reported at different rates which affect the stability of the system [384, 385, 389]. In this system Li passivation is due to the formation of a semiconductive crystal film in which the Li^+ cations are the basic current carriers [386].

Problems of voltage delays in cells which contain $LiAlCl_4$, $Li_2B_{12}Cl_{10}$ [387] or $Li_2B_{12}Cl_{12}$ have been discussed, and possible state of charge tests have been identified by Marincic *et al.* [388].

2.3.10. Polymeric carbon compounds $(CF_x)_n$

These have the ideal formula $(CF)_n \cdot (CF)_n$. Originally the system developed was $(CF_{0.25})$, which is a conductor [178], but later $(CF_x)_n$, where $x = 0.4 - 0.99$, a non-conductor, with a superior performance was developed [179 - 182].

In 1M $LiBF_4$–BL the cells have an open circuit voltage between 2.8 and 3.3 V, depending on the degree of fluorination, and an energy density of 300 W h/kg at low rates. Other electrolytes such as $LiClO_4$–PC [183, 184] and $LiAsF_6$–dimethyl sulphite (DMS) [185] may also be used.

The swelling of $(CF_x)_n$ is attributed to the precipitation of LiF in the pores of the positive electrode, and the change of $(CF_x)_n$ into amorphous and very fine particles [186, 187].

Although following the voltage delay, the voltage regulation of these cells is good, the cells are limited to low rate applications as they are poor conductors. They are suitable as miniaturised cells [390].

2.3.11. Sulphur dioxide (SO_2)

This is the most advanced lithium battery [188], and the use of SO_2 as a depolarizer in alkali batteries was discussed as early as 1948 [189]. Although the lithium and SO_2 have a large negative free energy of interaction, and would be expected to react rapidly, they do so only very slowly because of the $Li_2S_2O_4$ film which forms on the anode, and which is responsible for the voltage delay [190] and the long shelf life of these cells. The SO_2 also forms complexes with inorganic salts [191] which increase the conductivity of the organic solvent electrolytes [192].

Cells utilizing SO_2 have an open circuit voltage of 2.9 V and they can be discharged at high current or power levels, well beyond the capability of conventional primary cells [193] with an energy density of 330 W h/kg. Both current and power levels can be further increased by using cylindrical configurations of longer and thinner electrodes. Cells have been made [194] which discharge efficiently up to 7.5 A. Only the Zn/HgO cell, which has a high volumetric energy density, approaches the capability of this cell at 21 °C, but its performance drops off rapidly as the temperature is reduced whilst the performance of the SO_2 cell is high at −40 °C [193]. Its good performance at low temperatures is due to the conductivity of the SO_2 which only decreases from $5 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ at 25 °C to $2.4 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ at −50 °C [195].

The open circuit voltage of 2.9 V is maintained relatively constant until the capacity of the cell is almost fully utilized. Discharge is terminated by full use of the lithium (where lithium is the stoichiometric limiting electrode) or by deactivation of the carbon cathode (where this is the limiting electrode). Lithium limited cells are preferred as they do not produce toxic chemicals when the cells are fully discharged [196, 197].

The earlier types of cell consisted of Li|1.8M LiBr, An [10], SO_2 [23], PC [3] |C, but as the PC is one cause of the voltage delay, it is no longer used in modern cells [198, 199] which have been described in detail elsewhere [198 - 206]. Another improvement is the replacement of crimped seals by hermetic ones to reduce the capacity loss of 25% over 5 years to less than 2% [207].

If the cells are shorted 200 W are dissipated and high pressures, 500 - 600 psi, of SO_2 are generated. To prevent this hazard some cells are vented, and others have a slow delay fuse which deactivates the battery [208].

This cell represents an outstanding combination of high performance with complete safety under extreme hazard conditions, and it is now used in equipment requiring high energy and power density under a wide range of environmental conditions.

2.4. Electrolytes

Typically, an electrolyte consists of an organic salt (the solute), to provide the conductivity, in a solvent to ensure intimate contact with the electrodes.

The role of the electrolyte [209, 210] is to:-

(i) provide ionic conductivity between the anode and the cathode in the cell;

(ii) transport reactants and products to and from the electrode surface;

(iii) participate where necessary in charge transfer processes within the double-layer;

(iv) it must be chemically inert towards the electrodes, and have a good conductivity to prevent the build-up of a large internal resistance;

(v) it should dissolve the discharge products of the cathode, but not of the active material.

Account must also be taken of the role of the electrolyte in discharge reactions as the efficiency of the discharge is very much dependent on the particular solvent and, in some cases, the solute [211].

2.4.1. The solvent

As a high conductivity is essential, solvents of low viscosity and high dielectric constant (ϵ) have been used. A high conductivity implies that the solvent dissolves and ionizes the mineral salts whose ions carry the current [209].

Consider a salt AB and a solvent S.

$$n\mathrm{S} + \mathrm{AB} \longrightarrow n\mathrm{S}, \mathrm{A^-B^+}$$

These ion pairs dissociate forming free ions

$$n\mathrm{S}, \mathrm{A^-B^+} \rightleftharpoons n'\mathrm{S}, \mathrm{A^-} + n''\mathrm{S}, \mathrm{B^+} (n' + n'' = n)$$

$$K \text{ dissociation} = \frac{[\mathrm{A^-}][\mathrm{B^+}]}{[\mathrm{A^-B^+}]}$$

which is related to ϵ of the solvent

$$PK_\mathrm{d} = pK_0 + 0.43 \frac{Ne^2}{RT} \frac{Z_1 \times Z_2}{r_1 + r_2} \frac{1}{\epsilon}$$

where $PK_\mathrm{d} = -\log K_\mathrm{D}$, $\mathrm{PK_0}$ is a constant, Z represents the charges on the ions, r = the radii, and ϵ is the dielectric constant.

From this equation it can be seen that as ϵ of the solvent increases, the conductivity also increases. Solvents of low ϵ such as benzene and toluene do not normally form conductive solutions with conventional salts [209], but do form conductive systems with materials such as metal alkyls: compounds such as NaF $2\mathrm{Al(C_2H_5)_3}$ ($K = 7.87 \times 10^{-3}\ \Omega\ \mathrm{cm^{-1}}$) and benzene ($K = 1.1 \times 10^{-2}\ \Omega\ \mathrm{cm^{-1}}$) at a ratio of 10 moles of solvent to one mole of aluminium complex [212].

There are high conductivities for aprotic solutions containing large anions or cations or both, for example, morpholinium hexafluorophosphate. $\mathrm{LiClO_4}$ is very soluble in some organic solvents [213], and LiF is very soluble in BL in the presence of $\mathrm{BF_3}$.

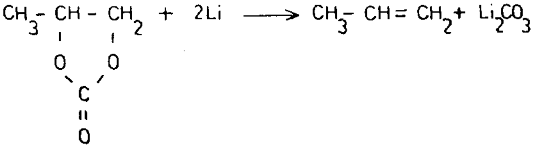
Because the solvent should be inert it should possess no mobile protons. Therefore, acids, alcohols, amides, amines, aldehydes, and phenols are automatically excluded.

Using these guidelines the solvents which can be used are limited but include:

Solvent		ϵ
nitromethane	(NM)	36
dimethylformamide	(DMF)	26.7
propylene carbonate	(PC)	64
dimethyl sulphoxide	(DMSO)	49
γ-butyrolactone	(BL)	39
isopropylamine	(IPA)	4.9

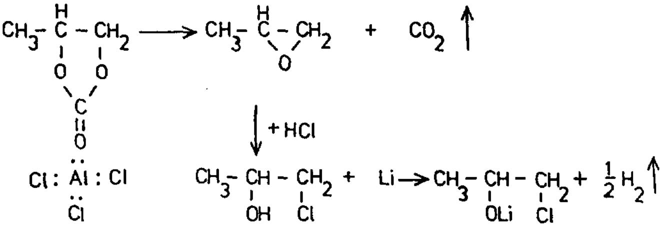
Some solvents show good ion conductivity if used together with a suitable solute, but only a few are stable *vs.* alkali metals. Two types of stability are required: chemical and electrochemical, and it is often the former which limits the battery performance. Because of this, aprotic organic solvents are extensively used [214, 398].

(a) Propylene carbonate (PC). The electrochemistry of PC in high energy density batteries has been discussed [215 - 220], and considerable emphasis has been placed on its use with lithium anodes. One reason for this was that lithium was thought to be stable in PC and that it could be used in a reference electrode [221 - 223]. It was shown, however, that the solvent's stability [224 - 227] was affected by heat, inorganic halides, acids and bases, metal oxides, and active proton-containing materials. Scarr [223] pointed out that PC decomposition is expected, and in the Li/Hg system it is rapid. The mechanism has been studied and is believed to be:



Only Dey [228 - 230] has connected the solvent's decomposition with electroreduction, but this does not seem to be the case as it is also reduced at Pb, Ag, Au, and Cu electrodes at potentials between +4 V and —1 V *vs.* K/Hg. His results may be explained by assuming that a reaction occurs between the lithium deposited in the graphite lattice at a potential of +1 V and the solvent [231]. This has been confirmed by Dousek [232].

Keller [233] suggested that the instability of PC in $AlCl_3$ in the presence of LiCl was due to solute–solvent interactions. $AlCl_3$ would exist predominantly as $AlCl_4^-$ provided sufficient Cl^- was present. It has been proposed that PC decomposes in $AlCl_3$ by the following mechanism [234].



Not enough HCl is produced to account for the above mechanism. An alternative scheme would involve the reaction of the oxide with $AlCl_3$, forming, in addition to the observed products, olefines and complex polymerization products. By adding excess LiCl, $AlCl_4^-$ is formed which results in a considerable reduction in the rate of solvent decomposition.

(b) Dimethyl sulphoxide (DMSO). This is a good solvent for organic and inorganic materials, being resistant to oxidation and reduction and having a high ϵ (49). The lithium salts are the most soluble, having a maximum conductivity at 1M LiCl [235, 236], and 1M $LiClO_4$ [236] which may result from ion pairing or from a large increase in the viscosity of the DMSO solutions. Compared with potassium, which reacts violently, and sodium, which reacts rapidly [237] forming sodium methanesulphenate, methylsulphinyl carbanion, methane, and dimethyl sulphide [238], lithium metal is unreactive with DMSO which is used as the solvent for the carboxymethyl cellulose binder in lithium batteries. It cannot, however, be used with some salts. In solutions containing NH_4PF_6, $NaPF_6$, and $NaSbF_6$ a vigorous reaction occurs, with H_2S evolution, and after two weeks the lithium anode (1 g) had completely dissolved in 20 cm^3 of the solution [239]. Compared with this, the rate of gas evolution in an LiBr–DMSO solution is negligible over a 16 h period [240].

(c) Dimethylformamide (DMF). This was not thought to be a suitable solvent [241] as it was believed to cause lithium corrosion and to induce strong polarization of the cathode during battery discharge which reduced the open circuit voltage to less than the theoretical value. It is now believed [242, 243] that these effects are related to the purity of the solvent, as pure DMF only reacts slowly with lithium [244]. The mechanism of formation of the products is still in dispute [245, 246]. Water is one of the main impurities, and may be removed by drying over molecular sieves for a few days [247 - 251]. The problems connected with solvent purification have recently been reviewed by Jasinski *et al.* [252].

(d) Isopropylamine (IPA). For some time, solvents with a high ϵ were preferred, but the use of IPA with copper halides has shown that basic aprotic solvents with a low ϵ (4.9) may be used. This solvent can be used because the reaction:

$C_3H_7NH_2 \longrightarrow C_3H_7NH + H^+$ is minimal.

If a supporting electrolyte is required it should be soluble in the solvent, but ion pairing has to be minimised [241]. Because of this, solvents of high solvating power, for example, THF, and tetrahydropyran (THP), are often mixed with solvents of low viscosity such as dimethoxyethane (DME) [253 - 256] or methylene chloride [257]. Propylene carbonate (PC) may be mixed with ethylene carbonate (EC) [258, 259], which has a high ϵ, or with nitromethane (NM) [260].

2.4.2. *Solutes*

Only a few inorganic salts show good solubility in organic solvents: the most common are $LiClO_4$, LiCl, LiBr, $LiBF_4$, $LiPF_6$, $LiAsF_6$ and $LiAlCl_4$. To increase the solubility of these salts, Lewis acids, such as BF_3 and $AlCl_3$, which form complexes and enhance the solubility of some of the rather insoluble salts [261 - 265], are added [241].

Water, again, is one of the major impurities which must be removed, and methods for drying these solutes have been described [266 - 271].

To develop better solutes, the interactions which can occur in the electrolyte have been examined. The most important interactions are:

(i) the electrostatic forces between the ions;

(ii) the Lewis acid–base interactions which involve cation reactions both with the solvent molecules and with the anions.

Mutual effects lead to the formation of solvated cations and solvated ion-associated complexes, and the effects these have on the properties of Li have been discussed in the literature [395, 396].

The conductivities (about 10^{-2} mho) and solubilities of these salts in organic solvents [272, 273] are at least an order of magnitude less compared with aqueous systems (0.2 - 0.3 mho and 0.5 mho in 7N potash) [241]. Because of the poor conductivity of the lithium electrolytes, lithium anodes with large surface areas (for example, spiral [274 - 276] or zig-zag configurations [277]) are used to compensate for the large internal resistance in the cell.

A new class of aprotic organic electrolytes in which lithium cycling is possible has been developed. Diethyl ether (DEE) and THF with $LiAsF_6$ give lithium cycling efficiencies $\gg 98\%$ and specular deposits of up to 10 C/cm^2 may be plated from these systems. Their kinetic stability is believed to be due to the formation of a film of lithium ethoxide [397].

Recently, solid electrolytes based on crown ethers have been employed, and as a result of the increased conductivity, a marked improvement in the performance has been observed [278]. Other solid electrolytes have conductivities two or three orders of magnitude less than organic electrolytes and can suffer from internal deposition of the metal phase (reduced ions). Further, if a critical voltage or current density is reached, then the electrolytes fracture, and the resultant voids reduce the conductivity even more [398].

2.5. *Separators*

The main functions of a separator are to:

(i) separate the anode and cathode materials;

(ii) prevent diffusion of particles between the cathode and the anode.

In addition, to be a good separator, the material must also:

(i) have a low resistance to the electrolyte flow;

(ii) be a good conductor in the electrolyte;

(iii) be easily wetted to maintain a current flow.

Cooper and Fleischer [279] have described techniques for the measurement of these parameters.

Some systems [280] use two pieces of non-woven Viskon as a separator, whilst others [281] use non-woven polypropylene or Teflon or PVC membranes [282]. These materials, however, have a high resistance and are permeable to the cathodic material thus causing the formation of passive films.

In the Li/CH_3OH system the life of the anode depends on the rate of diffusion of CH_3OH through the separator [282]. Separators which are stable in the electrolytes used, and which contribute relatively little to the internal resistance of the cell, are being developed to improve the battery performance [283]. They consist of either a lithium ion-conducting separator [284 - 287], or a perm-selective membrane which does not permit diffusion of the cathode into the anode compartment. Porous, sintered, flat plates of Y_2O_3 and MgO have also been developed [391].

2.6. *Film formation*

The stability of lithium depends on surface effects. Films of insoluble lithium salts [282 - 292] protect the bulk metal, and the corrosion rate depends on the solute [293]. These films do not lead to complete passivation of the anode as is typical with Group 2 and Group 3 metals. The stability of lithium in liquid electrolytes [294] is entirely due to the formation of these films. In cells with solid cathodes, the cathode does not contribute to the lithium film directly: the main contributor is the solvent.

The film thickness is controlled by altering the electrolyte variables so as not to passivate the lithium anode completely. This can be done empirically, and has led to the development of cells with good capabilities.

The kinetics but not the thermodynamics of the $Li \rightarrow Li^+ + e^-$ reaction are affected and the kinetics of the electrode reaction may be expressed empirically by the Tafel equation:

$$\eta = a + b \log I$$

which shows a linear relationship between the overvoltage, η, and the log of the current density, I.

2.6.1. *The effects of various materials*

Studies have been made of how various materials affect film formation.

(a) Propylene carbonate (PC). Jasinski *et al.* [295] and Dey [296] thought that the stability of lithium in PC was due to the formation of an Li_2CO_3 film formed by lithium decomposing the PC or by side reactions with impurities. Some authors [297, 298] used KPF_6 and $NaPF_6$ as electrolytes, which suggests a high passivity of the lithium electrode. The Li_2CO_3 film formed prevents further contact between the active lithium and the PC which prevents further decomposition. A reduction of the ions of the more electropositive alkali metal by cementation does not occur.

Kinetic measurements [299] of the $LiClO_4$–PC system have shown a dual Tafel behaviour which may be explained on the basis of film formation resulting from lithium reacting with the PC and not with impurities [299, 300] as previously suggested.

The morphology of the film has been studied by Dey [301] who found it to be a fine and granular structure.

The activation process is believed to be mechanical and not electrochemical [302] — being caused by anodic dissolution of the lithium from under the film at isolated spots.

(b) Tetrahydrofuran (THF). THF is used because of its low viscosity but methane production has been reported [303] in lithium cells of the type $Li/LiClO_4$, DME and THF mixtures. A gel-like massive film (possibly LiOH) has been observed [304] in Li/V_2O_5 and Li/Ag_2CrO_2 in 1M $LiClO_4$–THF. This film is not observed in pure Li–THF and we can therefore assume that the solid cathode participates in film formation [305]. It has been proposed that THF polymerises at the cathode [305], and "grows" by diffusion to the anode where growth ceases. This film may be the cause of serious voltage delays, as in the Li/V_2O_5 system. The characteristics of films of $[CH^{y+}(ClO_4)_y^{-}]_x$, where $y \leqslant 0.06$, which have conductivities of 10^3 ohm cm^{-1} have also been discussed [391].

Film formation occurs in most cells (except for the Li/CH_3OH system where lithium methanolate is formed), but in BL, DME, MF and acetonitrile (AN) the films have not been characterised.

2.6.2. Films in specific cells

(a) Lithium/sulphur dioxide. In the past PC was included in cells to aid film formation but, as this is instantaneous, it is no longer added [315, 316]. The film is responsible for the voltage delay at the start of the discharge and PC was found to increase the delay. The film is also responsible for the 5 - 10 year shelf-life of this cell [317, 318].

Scanning electron microscope studies [319] of the LiBr, AN, SO_2 film indicate that a dense, compact film of $Li_2S_2O_4$ is formed.

(b) Oxyhalides. In lithium cells involving the electrocatalytic reduction of inorganic oxyhalide electrolytes such as $Li/AlCl_4$, $SOCl_2$, $Li/AlCl_4$, SO_2Cl_2, there is no violent reaction because of the formation of LiCl which does not passivate the entire metal surface. The morphology of the film has been studied and it has been found to grow with time and increased temperature. The film growth is reduced in the absence of $LiAlCl_4$. Dey [320, 321] has shown that the voltage delay (discussed below) is much worse after storage at elevated temperatures.

(c) Lithium/pyromellitic dianhydride. Despite the solubility of the PDA cathode, the self-discharge rate is very low compared with other organic cathode materials. This might be due to a protective film which forms on the anode which is permeable to Li^+ but not to the PDA molecule [322].

2.6.3. Voltage delays associated with film formation

The problems of voltage delays and film formation are much reduced by a proper choice of electrolyte variables. In commercial cells [306] having hermetic seals, the problem of lithium films is minimal. The problem of voltage delay, however, which increases with storage life, still remains unclear.

Additives may be used which either promote [307] or reduce [308] formation of the passivating films. The discharge rate of lithium is improved by incorporating $NiCl_2$, $MgCl_2$, $ZnCl_2$, $HgCl_2$ or TlCl into the anode which removes the film [309]. Complexing additives such as 0.8 wt.% of hexamethylphosphotriamide [310] and 0.8 wt.% of hexamethylphosphoramide [311] also prevent the formation of the film. The voltage delay may also be alleviated by amalgamating the anode [312], or it may be coated [313] with an insoluble reaction product of the anode metal absorbing an inhibiting reactant such as CO_2, SO_2, O_2, NH_3, or N_2 saturated with respect to the water vapour. This film is only monolayers thick and it does not passivate the lithium anode.

The role of dissolved oxygen in $Li/AlCl_4PC$, $Li/AlCl_4NM$ has been investigated [314], and it was found that, when the partial pressure of the dissolved oxygen in these solutions was 0.2 atm, adsorption takes place on the anode preventing its reaction with the electrolyte.

$$(x + 1)Li^0 + O_2 \longrightarrow Li_x(O_2^{ad})Li$$

The Li_2CO_3 film forms above this film. The oxygen film causes no voltage delay; only the carbonate film does that. The problem of anode passivation in both primary and secondary cells has been reviewed by Scrosati [399].

2.7. Discharge mechanisms

Very little is known about the cathodic reduction or even the products [323]. The observed voltages often bear little, if any, relation to the simple reduction reactions.

Reduction	Theoretical OCV	Observed OCV	Reference
$HgF_2 \longrightarrow Hg + 2LiF$	3.4	1.6	324
$Ag_2O \longrightarrow Ag + Li_2O$	2.85	3.43	325
$Cu_2S \longrightarrow Cu + Li_2S$	2.3	2.3	326
$MoO_3 \longrightarrow MoO_2 + Li_2S$	2.2	2.8	327, 328, 329
$(CF_x)_n \longrightarrow C + LiF$	4.6	2.8	330, 331
$V_2O_5 \longrightarrow VO_2$	2.4	3.5	327, 328, 332,323

To account for these differences Whittingham [323] has proposed the formation of ternary phases, and has given evidence for their formation by topochemical reactions.

Below we give examples of some cathodic reductions which have been investigated.

2.7.1. *Lithium/halide cells*

(a) Lithium/aluminium chloride, propylene carbonate/silver chloride-($Li/AlCl_3$, PC/AgCl). In this system the anode polarized very little whilst the cathode polarized a lot [333]. The nature of this observed concentration polarization was found to be complex but can be represented by

anode

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

$$4Li + AlCl_4^- \longrightarrow 4LiCl + Al^{3+} + 4e^- \tag{2}$$

cathode

$$AgCl + e^- \longrightarrow Ag + Cl^- \tag{3}$$

$$4AgCl + Al^{3+} \longrightarrow 4Ag + AlCl_4^- \tag{4}$$

Reactions (2) and (4) are consistent with the ionic species observed by Hon [334] in a nuclear magnetic resonance study of $AlCl_3$ in AN, which may also prevail in the PC solution. For reactions (1) and (3) to occur the chloride must be in excess and be transported to the anode, and for reactions (2) and (4) $AlCl_4^-$ must be transported. If all the LiCl stays at the anode then the Cl^- or the $AlCl_4^-$ will diffuse at a slower rate. The effect of this will be to define a diffusion layer which is equivalent to the thickness of the LiCl, and which is set up due to the flow of current. When no current flows, ions diffuse into the diffusion layer, and this is observed as a gradual return of the open circuit voltage to the equilibrium value. It has been shown that the polarization can be reduced by adding excess electrolyte to dissolve the LiCl [332].

(b) Lithium/mercury fluoride (Li/HgF_2). It was found that the electrode polarization was, to a large extent, electrolyte dependent. By adding silver to the electrode the discharge voltage increased. This was found to be due to its preventing electrode poisoning by amalgamation of the mercury as it formed, and not to be due to the increased conductivity [335]. Acetylene black was added as a conductor.

(c) n-type lithium/cadmium fluoride (Li/CdF_2). The discharge of doped CdF_2 is better than the normal CdF_2 because the doped material offers an alternative discharge mechanism. In a porous electrode the electronic reduction mechanism [336] may supplement or supplant another process such as the reduction of dissolved Cd ions. For efficient use of this mechanism a low resistance contact at the semi-conductor–current collector interface must be used.

(d) Lithium/bismuth fluoride (Li/BiF_3) [338]. In this case, the discharge is known to be a two step process involving the formation of Bi and LiF [337].

The proposed reaction is:

$BiF_3 + 3Li \longrightarrow 3LiF + Bi$

If the above reaction is correct then the LiF and Bi would be in equilibrium with the BiF_3, and, as a result, the observed open circuit voltage of 3.13 V would be expected to be independent of the state of discharge. As this is not the case, the above mechanism is an over simplification.

2.7.2. Lithium/oxide cells

(a) Lithium/bismuth oxide (Li/Bi_2O_3). In this cell a two step discharge occurs. The first gives rise to metallic bismuth through a six electron transfer, and the second gives rise to Li_3Bi through another six electron transfer.

In Li/Bi_2O_3 cells in $LiAsF_6$–THF or $LiAsF_6$–BL the open circuit voltage exceeded 3 V. Even on low rates of discharge, however, it rapidly drops to below 2 V, indicating that the observed open circuit voltage is not the thermodynamic value of the Li/Bi_2O_3 couple. Furthermore, the observed specific capacities in $LiAsF_6$–THF (0.6 A h/g) and $LiAsF_6$–BL (0.53 A h/g) exceed those calculated on the basis of a simple reduction of $Bi_2O_3 \rightarrow Bi$ (0.345 A h/g). To explain this it has to be assumed that twelve electrons are involved in the discharge of each molecule of Bi_2O_3, which suggests that Bi forms compounds in which it is in the negative oxidation state. The discharge may then be written:

$6Li + Bi_2O_3 \longrightarrow 2Bi + 3Li_2O$

$2Bi + 6Li \longrightarrow 2Li_3Bi$

$12Li + Bi_2O_3 \longrightarrow 2Li_3Bi + 3Li_2O$

On the basis of this reaction a theoretical energy density of 835 W h/kg was calculated, although in practice the $Li/LiAsF_6$–THF/Bi_2O_3 cell only has an energy density of 200 W h/kg. It has been suggested [339] that the formation of a ternary nonstoichiometric phase is responsible for this lower than calculated energy density, but it has not yet been identified.

(b) Lithium/titanium dioxide (Li/TiO_2). In this cell the discharge is known to be [340]:

$$Li + Ti(IV)O_2 \longrightarrow Ti(III)(Li^+)O_2 \xrightarrow{\text{rearrangement}} LiTiO_2$$

The differences between the theoretical OCV (1.1 V) and the practical open circuit voltage (2.9 V), and between the anatase and rutile TiO_2 are points of interest in this cell. The *a*, and *c* dimensions of the two forms are:

	A	*C*
Anatase	3.79	9.51 Å
Rutile	4.59	2.96 Å

The differences are believed to be linked with the longer *c* dimension in the anatase form. Because of this wider separation, the lithium ions can diffuse into the matrix of the anatase lattice more easily and, as a result, a cell of this type has a higher working voltage, but is more readily discharged in 1M $LiClO_4$–PC compared with the rutile form.

(c) Lithium/manganese dioxide (Li/MnO_2). It was shown [341] that cells using MnO_2 discharged by the reaction:

$$2Li + 2MnO_2 \longrightarrow Mn_2O_3 + Li_2O$$

Based on this reaction the open circuit voltage should be 2.69 V. It is almost 3 V, however, and the presence of Mn_2O_3 or Li_2O could not be confirmed by X-ray analysis. Because of this the reaction:-

$$Li + Mn(IV)O_2 \longrightarrow Mn(III)O_2(Li^+)$$

was proposed and verified by X-ray analysis.

(d) Lithium/vanadium pentoxide (Li/V_2O_5). The postulated discharge in this case is [343]:

$$V_2O_5 + 4Li \longrightarrow V_2O_3 + 2Li_2O$$

To account for the theoretical open circuit voltage (2.11 V) being less than the observed value (3.5 - 3.75 V), a topochemical reaction involving the incorporation of lithium into the V_2O_5 has been proposed for the first plateau. X-ray analysis supports this idea. The second and third plateaus are harder to characterise but may involve the formation of V_2O_4 and V_2O_3.

(e) Lithium/silver oxide (Li/AgO). The simplest mechanism suggested for Li/AgO is [344]:

$$Ag_2O + 2Li \longrightarrow 2Ag + Li_2O \qquad (1)$$

$$AgO + 2Li \longrightarrow Ag + Li_2O \qquad (2)$$

which could occur stepwise:

$$2AgO + 2Li \longrightarrow Li_2O + Ag_2O \qquad (3)$$

but the open circuit voltage and the voltages on load indicate that these reactions do not occur. The discharge can, however, be explained if we assume that amorphous ternary phases are formed through Li^+ insertion [345] according to the reactions

$$Ag_2O + xLi \longrightarrow Li_x Ag_{2-y}O + yAg$$

$$AgO + xLi \longrightarrow Li_x Ag_{1-y}O + yAg$$

The decreasing open circuit voltage indicates that no equilibrium is reached between the products and the reactants [346]. Half of an electron is involved in the initial reduction of both oxides. After complete reaction of the oxides, the reactions are thought to be maintained *via* the ternary phases.

$$Li_xAg_{2-y}O + x_1Li \longrightarrow Li_{(x+x_1)}Ag_{(2-y-y_1)} + y_1Ag$$

$$Li_xAg_{1-y}O + xLi \longrightarrow Li_{(x+x_1)}Ag_{(1-y-y_1)}O + y_1Ag$$

X-ray analysis seems to confirm these schemes.

The insertion of lithium ions into the compact [347] Ag_2O, AgO lattices causes distortion and bond breakage which is believed to prevent reversibility.

2.7.3. Sulphides and selenides

(a) Lithium/titanium sulphide (Li/TiS_3) and lithium/niobium selenide-(Li/$NbSe_3$). Both these compounds undergo topochemical reactions with lithium on discharge forming compounds of the type Li_3MX_3. The reaction is completely reversible for $NbSe_3$ but only partly reversible for TiS_3. The basic chain structure of these compounds is maintained on lithiation. Reversibility has been equated with the maintenance of the microstructure. In the case of TiS_3 there is evidence that it changes from a trigonal prismatic to an octahedral coordination [348] on lithiation, and that this change is irreversible.

2.7.4. Lithium/oxysalts

It is believed [349, 350] that the discharge of oxysalts results in the displacement of the metal by lithium, and X-ray analysis seems to confirm this. The main discharge plateau caused by this mechanism is followed by others which are harder to interpret. Explanations of the full discharge vary from possible intercalation in the oxysalt matrix [351] to reduction of the oxysalt anion [352, 350].

For Ag_2CrO_4 the proposed reactions are [353, 354]:

$$Ag_2CrO_4 + 4Li \longrightarrow 2Ag + CrO_2 + 2Li_2O$$

$$Ag_2CrO_4 + 2Li \longrightarrow 2Ag + Li_2CrO_4 \qquad (1)$$

Four equivalents/mole of Ag_2CrO_4 were realised in the cell, whereas only two would be expected from eqn. (1). As the thermodynamic potentials calculated from the above reactions do not correspond to the experimentally observed values these reactions are not valid. It has been shown [355] that Ag_2CrO_4 is reduced *via* different routes, depending on the discharge current density. At low current densities reduction to Ag occurs, whilst at high current densities $Li_xAg_2CrO_4$ is formed which decomposes forming Ag, lithium chromate and silver chromate. More recent evidence [356] seems to suggest that after all the silver(I) has been reduced to silver(0), electrochemical formation of Cr(V) then occurs and this then reacts with silver(I). At high rates of discharge the overall rate of reduction is limited by the rate of reaction between Ag(I) and Cr(V), thus causing a drop of 0.4 V to the second plateau. These results account for the good performance of Ag_2CrO_4 in lithium batteries.

2.7.5. Lithium/polymeric carbon compounds (Li/$(CF_x)_n$)

The proposed discharge mechanism is [357, 358]:

$$\frac{1}{n}(CF_x)_n + Li \longrightarrow \frac{1}{n}(C)_n + LiF \qquad (1)$$

Based on the free energies of formation of LiF and $(CF_x)_n$ the theoretical open circuit voltage should be 4 V whilst in practice it is 2.8 V. To account for this it has been suggested that lithium diffuses between the layers of the graphite lattice to react with the F, forming a ternary compound of the composition CLi_xF where $x < 1$. This would then disproportionate to give LiF and graphite.

The observed open circuit voltage corresponds to the reaction

$$Li + \frac{1}{nx}(CF)_n \longrightarrow \frac{1}{x}(CLi_xF) \qquad (2)$$

The variation of the open circuit voltage with the depth of discharge of the $(CF_x)_n$ cathode corroborates reaction (2). From eqn. (1) the open circuit voltage would be expected to be independent of the depth of discharge, which is not the case [358].

2.7.6. Lithium/sulphur dioxide (Li/SO_2)

The cell reaction in this system has been established [359]:

$$2Li \longrightarrow 2Li^+ + 2e^-$$

$$2SO_2 + 2e^- \longrightarrow S_2O_4^{2-}$$

$$2Li + 2SO_2 \longrightarrow Li_2S_2O_4$$

The $Li_2S_2O_4$ is an insoluble product which precipitates in the porous cathode and eventually causes passivation of the active carbon surface before the available SO_2 can be totally consumed [360].

2.8. Hazards

The possible hazards involved in the use of lithium cells have been thoroughly investigated and reported [361]. The cells have been tested under various hazard-inducing conditions, but in all cases the presence of the safety vent has virtually eliminated the possibility of spontaneous explosions. In general, therefore, it can be concluded that the potential hazards are no more than those involved in the use of alternative cells already being commercially exploited.

2.9. Applications

The SO_2 cell has found extensive use in military applications [362] because it can discharge at high current densities — well beyond the capability of the conventional primary batteries — and can be used at low temperatures. Applications include:-

(i) Transmitter/receivers: it is preferable in combat where it has weight advantage and a better performance compared with the mercury battery which weighs three times as much (1.5 kg compared with 0.59 kg for a lithium cell).

(ii) Missile firing systems where heavy current pulses at the $C/2$ rate are required. It gives a better performance than the Ni/Cd battery at all temperatures, giving ten times as many firings (14 A for 100 ms).

(iii) In missiles on launch it can withstand a high shock — up to 15 000 g.

(iv) It is replacing Mg/AgCl sea water activated batteries in sonobuoys [363].

(v) It is replacing magnesium and mercury batteries in E.L.T. systems because of its low temperature application.

(vi) It can be used in memory protection in random access memory circuits.

Apart from SO_2 and the oxyhalides, there are a number of other materials — chiefly $(CF_x)_n$, V_2O_4, MoO_3, CuO and Ag_2CrO_4 — which are suitable for practical applications.

The V_2O_4 and $(CF_x)_n$ cells are also being developed for special military purposes [364, 365], but the $(CF_x)_n$ cell is suitable for many other applications.

The AgI and the $AgCrO_4$ cells are suitable as small size, high energy, primary power sources, and are used as power sources for pacemakers. Considering the good operational capabilities of the oxysalt batteries under high energy drains the range of utilization of these cells may be extended to other applications where high pulses are required, for example, watches.

The MnO_2 system has found widespread application as a power source in watches, calculators, cameras, hearing aids, cassette tape recorders, radios and in volatile memory protection circuits, whilst the CuO battery has the advantage that it can replace Leclanché-type batteries directly without modification because its working voltage is 1.3 V.

Because of their good charge/size ratio these batteries are being developed to power motors (up to 2000 W h). A conventional system would weigh 500 lb, whereas the Li/SO_2 system would weigh under 100 lb. It is unlikely, however, that many systems will be marketed until a secondary lithium battery has been developed.

2.10. Conclusions

The primary lithium cells discussed here are new and useful devices for the storage of electrical energy. They are suitable for use in applications requiring high energy densities, high current delivering capabilities, and effective operation over a wide temperature range. They have been the subject of an intense research effort in recent years and show much promise for being developed into light weight, reliable, high energy density power sources for a number of military and non military applications. For most operations, the prerequisites for a cell are:

(a) high energy density;

(b) long shelf life — in excess of 5 years;

(c) light weight.

Lithium primary cells fit these criteria well as they can possess:

(i) high practical energy densities — around 290 W h/kg at room temperature in the case of the Li/SO_2 primary cell, which only decreases to 130 W h/kg at −55 °C at 10 mA;

(ii) an ability to operate efficiently under continuous current drains ranging from mA to about 7 A;

(iii) stable on load voltages;

(iv) a range of single cell voltages between 1.2 and 3.8 V, depending on the particular system chosen.

The basic characteristics of lithium cells with both organic and inorganic electrolytes have been described. Several different combinations of cathode materials and electrolytes have been considered and it has been shown that lithium primary cells have a high discharge rate capability and excellent performance at low temperatures.

The high conductivity and low viscosity of some of the electrolytes, especially those based on sulphur dioxide and thionyl chloride, over a wide range of temperatures, together with their stability in contact with the lithium anode on storage, and apparent compatability with other cell components, has led to the development of a group of lithium primary cells with superior characteristics.

Despite recent advances in the area of both solid and liquid cathode materials, however, it is evident from their behaviour that many problems remain to be solved.

The most important of these are:

(a) Lithium anode passivation during storage. This has been a major problem in the full utilization of these cells. The passivation manifests itself as voltage delays and voltage depression during cell discharge. Specific solutions to this problem have been sought through electrode and electrolyte modification.

(b) The discharge mechanism. In many cases the discharge mechanism is not understood, and it is not always a simple, straightforward reduction, but may involve topochemical, rearrangement, or insertion reactions.

(c) The effect of the cell components on its performance. Significant improvements have been brought about in the performance of these primary cells through the use of newly developed components and materials [400]. The manner in which these improvements arise is not always clear.

3. Secondary lithium cells

3.1. Introduction

Since it is hard to recycle lithium efficiently, primary cells developed faster, and by now many good systems are on the market. Nevertheless, secondary lithium cells have been studied for some time [401], and, as a result of some new discoveries [402] — such as new organic solvent/Li salt combinations — the lithium electrode can be recharged with high efficiency. Examples of these new systems are the EIC system [403], 2-methyl THF/$LiAsF_6$, and the EXXON electrolyte [404] (1,3-dioxolane/$LiClO_4$) although, as the 1,3-dioxolane detonates on impact, it has already been abandoned [405].

Many rechargeable cathode materials have been developed [406] and the most promising ones are the solid state cathodes which undergo intercalation or topochemical reactions with lithium. Typical of these is TiS_2, and a Li/TiS_2 cell utilizing a 2-methyl THF/$LiAsF_6$ electrolyte [407] can undergo 200 deep discharge cycles but it has the disadvantage of a relatively low energy density.

The problems are that not only does the lithium recycle poorly, but in many cases the cathodes are equally bad: in most cases they are not fully reversible [408]. This limits cycle life, and the performance would be much improved by a truly solid state redox cathode.

Extreme examples of irreversible cathodes are provided by the sulphur oxides and related compounds — once these are reduced oxidation to the initial state is impossible.

3.2. Mechanism and structure

The reaction of inorganic cathodes in lithium cells is either by insertion or by displacement. Displacement reactions are preferred to insertion reactions because they can react more reversibly.

Only in the last ten years has the electrode reaction been understood. Most of the oxides, sulphides, and selenides of the 'early' transition metals reacted by incorporating the lithium into the crystalline lattice, forming ternary phases, for example, Li_xTiS_2 [409, 410]. At various times this type of reaction has been called insertion, intercalation, or topochemical. Titanium disulphide and a few other cathodes can be cycled many hundreds of times at high current densities, but the other cell components cannot be recycled as many times. No electrolyte is presently known that is high rate — (10 mA cm^{-2}), safe, and can plate out lithium metal at efficiencies better than 99.9%. This is a reverse of the situation pertaining a decade ago when the cathodes were the weak link in the development of lithium secondary cells.

Although the mechanism of discharge of many cathodes in secondary lithium cells is now being unravelled, there is still no battery that is both technically and economically viable for a long-lived, multi-cycled battery.

3.3. Basic problems

Lithium may be plated with about 100% efficiency in PC [411], but it can't be stripped well, especially after standing the deposit in the electrolyte. This is due to the metal deposit being electrically isolated from the conductive substrate and becoming more and more dendritic. The matter is made worse by the reactivity of the solvent. Up to now it has been difficult to find a solvent that is thermodynamically stable. To sustain the electrolyte solubility and conductivity, the solvent must be polar.

Lithium films, which are responsible for the long term stability of primary cells, are a serious problem in the recycling of secondary cells. $LiAsF_6$ is good because it forms a "desirable" film and may be the first of others to come.

3.4. Lithium cycling in secondary cells

Lithium cycling may be improved by modifying the lithium/solution interface and its reactivity. In theory this can be done in numerous ways:

(i) by the use of surface active additives — levelling agents,
(ii) by the use of surface active additives — precursors,
(iii) by the use of alloying substrates,
(iv) by the use of internally generated scavengers,
(v) by rigorous electrolyte purification.

3.4.1. Levelling devices

These substances control the damaging intergranular corrosion process. In PC-based electrolytes, the addition of surface active materials may have a beneficial effect on the lithium morphology [412], albeit at low current densities <0.1 mA cm^{-2}. Apart from the benefit in its morphology an improvement in the lithium adherance has also been reported when rhodamine B (sodium salt) and disodium fluorescein is added to $PC/LiAlCl_4$ [413].

3.4.2. Precursors

In this case it is believed that compounds such as SO_2, $SOCl_2$ compete with the solvent for the surface and form a 'desirable' type of film. The term 'desirable' refers to a possible monolayer which may be formed, or one which is lithium ion conducting but at the same time impermeable to the solvent molecules. Carbon disulphide, $PSCl_3$, $POBr_3$, $PNBr_2$, SO_2, N_2O have all been used as precursors in PC/1M $LiClO_4$ [412] and MA [414]. Of these CS_2 was found to be the worst precursor material as it forms a resistive film. $PSBr_3$ and SO_2, however, were both good, giving cycling efficiencies of 84.5% and 79.8%, respectively.

Many substances can form films instead of PC itself, which can give cycling efficiencies of about 85% in 1M $LiAsF_6$. This suggests, perhaps, that PC adsorption on certain crystal faces still controls some basic aspects of the morphology of the deposit. By itself, lithium cycling efficiency in $LiAsF_6$ is 85.2% but on the addition of 0.01M $POBr_3$ in $LiClO_4$, the efficiency falls to 75.8%. This suggests that the AsF_6^- and $POBr_3$ compete for the same sites and act in the same way. Although the cycling efficiency is enhanced initially, it eventually falls after about ten or twenty cycles. The loss of efficiency is because of granules of lithium that are encapsulated by insulating films of PC/Li reaction products, thus severing the electrical contact with the substrate. The rate of capacity loss can, however, be decreased by additives. These form lithium ion conductive films on the deposit, thus allowing deposition onto the granules and their growth into larger granules. In the long term though, an insoluble Li/PC film is formed over the lithium ion conducting film thus limiting the use of PC in secondary lithium cells [415].

The efficiency of cycling lithium on Ni in MA/1M $LiClO_4$ containing less than 100 ppm H_2O was less than 10%. When small amounts of NM or SO_2 were added, the efficiency improved markedly.

MA + SO_2 or NM is better than PC because more cycles may be realized before cell failure. The amount of lithium loss on open circuit voltage is minimal due to the greater solubility of MA/lithium reaction products [414], which allows a greater opportunity for build up of additive-induced conductive fibres on the metallic deposit.

3.4.3. *Alloying substrates*

Good cycling of the lithium may be achieved by alloying it, especially with aluminium.

Alloying works because:

(i) the more anodic potential of the alloy lessens the driving force for solution reduction;

(ii) it dissolves the lithium deposit into the alloying substrate, thus eliminating the possibility of undercutting the deposit by reaction with the solution.

The effect is only observed for very thin plates. For electrodes having a practical thickness, a high area substrate is required as the volume changes which occur during the formation and dissolution of the alloy tend to destroy the substrate.

The improvement in the lithium cycling efficiency which may be obtained by substituting an aluminium substrate for a lithium substrate can be explained by the morphological and kinetic changes that occur to the lithium electrode in the molar solution of $LiClO_4$/PC.

3.4.4. *Scavengers*

If an inert salt is added to the electrolyte, for example, LiBr, then on overcharge, or if we use a negative limited configuration, on overdischarge, the scavenger Br_2 is produced at the anode. It would dissolve encapsulated lithium and, since there would be no other lithium metal available, we could expect high efficiencies. The redox potential of the scavenger must be above that of the positive electrode, *i.e.*, in the case of the LiBr, Br^- will be the normal, non-corrosive form. In practice, the use of scavengers has proved a viable approach [416], but to get the best results:-

(i) the scavengers and the lithium salts of their reduction should be soluble in the solvent;

(ii) the redox potential of the scavenger must be above that of the positive electrode;

(iii) the scavenger/redox process must be simple, *e.g.*, Li/I_2, $LiBr/Br_2$, chloranil, fluoranil, lithium polysulphide and ferrocene/ferrocinium.

3.4.5. Electrolyte purification

This is a necessary, but in itself an insufficient, condition for obtaining high lithium cycling efficiencies.

3.5. Solvents

Lithium has been studied both in organic and in inorganic esters. Initially, empirical rules were used to connect the structure of the material: alkyl radical length, cyclic or acyclic with the lithium.

The dimethyl, diethyl and propylene sulphates, and trimethyl and trimethyl phosphates are solvents in which the Li/Li^+ system is both rapid and reversible. In these solvents and also PC, exchange reactions such as

$$R_2SO_4 + 2MX \rightleftharpoons M_2SO_4 + 2RX$$

occur.

Tetrahydrofuran is far too reactive for use in secondary cells. Even very pure THF reacts rapidly and with the lithium it has been found that 2-MeTHF/$LiAsF_6$ is a superior solvent for lithium cycling [417]. Similarly, 2-MeTHF and 2,5-dimethylTHF are both superior to either THF or 3-MeTHF. If, however, the 2-MeTHF is impure, then rapid corrosion occurs due to the presence of butylated hydroxytoluene (BHT) — a stabilizer added in the manufacture of MeTHF — which corrodes the lithium. The system can be tested by cycling the lithium to and from a conducting substrate remembering that the salt and solvent we choose should be compatible with the lithium, and that the electrolyte is inert. If such tests are done with THF-based electrolytes, on the tenth cycle 80% of the lithium plated is encapsulated by films and lost to anodic dissolution. In 2-MeTHF only 7% is isolated and therefore this is the better electrolyte with less degradation for a given number of cycles. It also has less effect on the morphology of the plates which are less dendritic than those with THF. Even in 1.5M $LiAsF_6$/2-MeTHF, however, efficiencies as high as 97.4% were obtained when the current was lowered to 0.9 mA cm^{-2}, presumably as a result of the improved lithium plate morphology at lower current densities.

Another problem associated with secondary lithium cells is the poor solvent stability on open circuit. After 96 h, 70% of the lithium plated was still available in the 2-MeTHF, but in the THF, all the plated lithium was isolated in 48 h, *i.e.*, an average rate of 1.1 μA cm^{-2} for the THF and 10 μA cm^{-2} over 26 h for 1M $LiAsF_6$/PC. In the case of $LiAsF_6$/THF, however, "recontacting" is observed. In this process lithium, which has become electrochemically insulated from the anode, becomes reattached, and thereby available for anodic dissolution. This recovery occurs on open circuit voltage [417]. In contrast to these findings, it has also been pointed out that THF is the least reactive towards lithium at elevated temperatures and gave the best cycling efficiencies. These efficiencies could be further improved by ageing the electrolyte at 71 °C and by adding O_2 or N_2 to the electrolyte. Carbon dioxide cannot be used because it causes cell failure. Tetrahydrofuran also shows a recontact phenomenon — whereby previously isolated lithium could be recouped in subsequent cycles. This could be explained by the breakdown of the films on the encapsulated lithium.

In primary cells, film formation can be beneficial, but in secondary cells it can be a serious problem. If the lithium is not plated smoothly, then filming is enhanced. As a result of this, the lithium granules may become encapsulated and cannot be discharged. This process can eventually lead to rapid cell failure.

3.6. Cycling behaviour in specific electrolytes

The key technical problem preventing the realization of high energy density secondary lithium cells which function at room temperature is the unacceptable cycling behaviour of the lithium electrode [418 - 421]. Another reason is the reactivity of the solvent towards the lithium.

Polar solvents may not be used because of the molecular dipole [422]. In order to retard the lithium/solvent reactivity, cyclic ethers have been used. These may be used because the C—O bond is far less polar than the C=O bond.

Not many successful electrolyte systems have been developed, but they include those based on THF, dioxolane, methylacetate (MA) and on PC.

(a) Tetrahydrofuran based electrolytes. Koch was the first person to identify 2-MeTHF–$LiAsF_6$ as a promising organic electrolyte for secondary lithium cells. It is good because of its low reactivity towards the lithium metal and this could be due either to the high purity of the salt or to the stabilizing property of the AsF_6^-. It has been noted, however, that THF and $LiAsF_6$ react at the lithium forming a brown coating [423]. The impurities which are believed to cause this colour change react faster with the lithium electrode than with the electrolyte [424].

When taken together, these results indicate the importance of films in ultimately determining the rate of the lithium/electrolyte reactivity. The specific nature of the reaction of lithium with THF-based electrolytes, the kinds and distribution of products, and the mechanism accounting for their formation is not fully understood [417].

By using certain additives we could form a protective film between the lithium and the electrolyte. This would add a diffusional barrier in series with the kinetic barrier. In order that this approach should work, the molecules of the additive must react more with the lithium than the 2-MeTHF. Furthermore, the film must be ionically conducting, and be stable in plating and stripping operations. In this respect, the alcohols, and in particular the polyethylene glycols (PEGS), have been reported to form films which are ionically conductive [425], and the system Li in 0.5M $LiAsF_6$/2-MeTHF electrolyte containing 2M 2-methoxyethanol has been reported to give over 900 cycles with efficiencies greater than 90% [426].

(b) Dioxolane based electrolytes. Originally, the Li/TiS_2 cell contained $LiClO_4$ as the electrolyte, but as this is explosive, it is no longer used [426,

427]. The potential scope for anion structural modification is unsurpassed in a complex (multicomponent) anion and a particularly rich synthetic chemistry for lithium tetraorganoborate salts has been well documented [428 - 430].

$LiB(CH_3)_4$ is one of the complex anion salts which is very stable and has a high conductivity in dioxolane. It has a tetrahedral symmetry and ionic dimensions [431] which closely resemble those of $LiClO_4$ [432]. Li/TiS_2 cells with $LiB(CH_3)_4$ have been shown to be capable of continuous discharge (5 mA cm^{-2}) and charge (1.25 mA cm^{-2}) cycling.

In general, the solutions are stable, but in TiS_2 we get anion $[B(CH_3)_4^-]$ oxidation with concomitant formation of Li_xTiS_2 ($x < 1$), and after a long time $(CH_3)_3B$, CH_4 and CH_3CH_3. Therefore, this combination is not suited to long term use in Li/TiS_2 cells.

(c) Methyl acetate (MA) based electrolytes. The cycling efficiency of the lithium electrode in $LiAsF_6$ and $LiClO_4$/MA electrolytes with, and without, the addition of SO_2 has been studied by Dampier and Brummer [433]. They found that the best cycling efficiencies, >90%, were obtained in 1M $LiAsF_6$/MA. It was also found that stripping efficiencies at low current densities gave a lower lithium recovery.

(d) Propylene carbonate based electrolytes. In $LiClO_4$/PC electrolytes plating efficiencies tend to 100% [422]. Most of the inefficiencies that result occur on the stripping process, following which, most of the unaccountable lithium remains as insulated lithium on the electrode [434]. Under open circuit conditions the lithium oxidation rate is ten times less than the capacity loss rate.

It was also found that the cycling efficiency also falls with the number of cycles. This is believed to be due to blockage of portions of the substrate with reaction products and accumulation of insulated lithium [415].

As is the case with primary cells, a positive, limited system is best for achieving highest energy density combinations. In the case of soluble positive systems, in which much of the lithium capacity is lost as self discharge, *e.g.*, Li/Br_2 [422], a negative limited system is feasible and perhaps best.

3.7. The anode

At present we are unable to get high energy density cells because of the reactivity of the lithium, which leads to the formation of passivating layers on cathodically deposited lithium during both charge and storage periods. These layers are responsible for the failures observed in trying to get 100% dissolution efficiency of the lithium. The surface state of the anode influences the discharge performance of liquid electrolyte secondary systems since it affects the rechargeability [435]. This is why, in some cases, they are still being developed. Several positives have been characterised and their properties identified but, in many cases, the properties of the anode render the positives useless.

In trying to overcome these problems, various approaches have been tested including:

(i) cleaning the electrolyte,

(ii) the use of certain additives,

(iii) altering the solvent reactivity by structural modification [415, 424, 436].

Although some good responses have been obtained using the above techniques, the overall response is still poor. As a result, the use of lithium incorporation in metallic lattices has been suggested. This results in a decrease in the chemical activity of the electrode [437 - 439].

Promising results have also been obtained with an aluminium substrate [440], and a comparison of the lithium deposited on aluminium and on a lithium substrate showed that:

(i) PC decomposition proceeds in the same way with both electrodes, yielding a plastic and porous layer;

(ii) the lithium incorporation rate on an aluminium substrate is not fast enough to avoid the formation of a passivating layer. The rate of incorporation is, however, sufficiently high for cathodic charge densities to be ten to twenty times larger than when a lithium substrate is used without the formation of dendrites, and without a thick passivating film developing, as is seen when lithium is thus reduced;

(iii) lithium incorporation into an aluminium substrate does not involve a prohibitive penalty voltage (~0.4 V). This is homogeneous enough to obtain a very large increase in the active part of the electrode surface involved in the charge transfer process.

It is believed that the more satisfactory results obtained during cycling with an aluminium substrate compared with those obtained with a lithium substrate is mainly due to the limited diffusion in the bulk of the electrode. Therefore, for further improvements, we have to improve the diffusion rate of the lithium by changing the structure of the substrate.

Lithium may be deposited from $LiClO_4$/PC and $LiAlCl_4$/PC with current yields approaching 100% if calculated from hydrogen evolution with water [441]. The immediate redissolution of the anode, however, is only about 80% efficient, the loss in efficiency being due to the presence of dendrites and poor adhesion [442] rather than to reaction with the solvent.

On storage, the anodic efficiency decreases drastically [443]. In an attempt to improve matters, use has been made of microporous [443] separators or of additives which either:

(i) give a smooth deposition of lithium,

(ii) alloy the lithium to reactive substrates,

(iii) use porous lithium electrodes in electrolytes containing anions which form insoluble lithium salts.

The surface of the anode becomes more pitted with increasing current densities. This may be minimised by doping with tetraglyme to form Li/nBu_4Cl in $LiClO_4$/PC. If this is done then the lithium deposits are compact.

Another problem which has dogged the development of lithium secondary cells is the growth of dendrites [442]. To try and minimise this problem, Li/Al electrodes which, under certain conditions have potentials close to that of the lithium electrode, may be used — reducing the voltage penalty required to minimise the dendrite problem. One reason for the dendritic formation is that freshly plated lithium is very reactive and as such ions react with impurities causing dendritic plating. We have already mentioned how this situation may be improved by solvent purification or by alloying with aluminium. Matters could also be improved by forming intermetallic compounds.

A Li/Al couple has the benefit that it is readily reversible in organic electrolytes. Lithium/aluminium electrodes are already being used with molten salt cells, *e.g.*, Li/Al FeS_2 cell in LiCl/KCl eutectic [444]. Recently it has been reported that the wet stand behaviour of cathodically formed Li/Al alloys (compared with lithium deposited on inert substrates) is considerably improved [445]. As a result, low self-discharge rates should be feasible which, in the case of Li/Al, is most probably due to the higher overvoltage for PC reduction on the electrode. Extensive cycling, however, is not possible; the aluminium shows degradation of aluminium foil with the formation of loosely adherent powder.

Porous Li/Al electrodes were fabricated by the pyrometallurgical technique [439] and incorporated into TiS_2 cells. On successively recharging these cells it was found that the Li/Al voltage approached that of the lithium electrode. This is believed to be associated with a structural change in the Li/Al electrode.

$$\mathrm{Li/Al}_\beta \rightleftharpoons \mathrm{Li/Al}_\alpha + \mathrm{Li/Al}_\beta$$

The α structure is lithium deficient whilst the β form allows fast diffusion of the lithium ions into its matrix. These electrodes are still affected by dendrite formation at high rates of charging or overcharging. The electrode reaction is

$$\mathrm{Al} + x\mathrm{Li}^+ + xe^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} \mathrm{Li}_x\mathrm{Al}$$

The rate of lithium insertion into the aluminium matrix can be high enough to prevent dendritic growth.

Electrochemical impedance measurements associated with the polarization curve data [446] indicate that most of the surface is active, giving rise to current densities of about 17 mA cm^{-2}. These studies have also demonstrated that the diffusional process in the passivating layer and in the bulk of the electrode is responsible for the limited lithium cycling performances when using an aluminium substrate.

The difficulties with the dendritic depositions of lithium may be circumvented if a lithium electrode of the second kind is used [447], *e.g.*,

$Li/nBu_4ClO_4 + (NBu_4)_2SO_4$/dimethyl sulphate/$CuSO_4$ [448]

More recently, the concept of an all solid composite electrode has been presented [449]. This would take the form of a finely dispersed reactant, *e.g.*, Li_3Si mixed in a solid, mixed, conducting matrix $Li_{2.6}Sn$. Such a cell could be charged and discharged without much loss in capacity. The polarization values are typical of those obtained on highly porous electrode systems in molten salt electrolytes.

In the search for high energy density, secondary lithium cells, complete reversibility has been shown [450, 451, 452, 419] in some cells where the cathodic mechanism is by intercalation or topochemical reaction. Problems remain, however, due to the lithium electrode, which has poor stripping/plating efficiencies in organic electrolytes [453, 434, 415]. By replacing the lithium anode by another intercalating electrode having a different lithium activity a cell of the type Li_xWO_2/Li_y TiS_2 [454] has been developed which, although giving a lower working voltage, can be recharged more, and which, on prolonged recycling, gives no serious indications of cell deterioration such as an increase in the internal resistance.

3.8. Cathode materials

Until recently, a repeatedly rechargeable lithium cell could only be realised using a large excess of lithium metal, but it had poor wet stand stability.

The cathode materials initially investigated consisted of the insoluble transition metal salts which formed the corresponding lithium salts on discharge [455]. These cathodes are, however, not completely satisfactory. The main groups of positives that have been studied are:

(i) sulphides and selenides
(ii) sulphospinels
(iii) transition metal oxides
(iv) organic cathodes
(v) other cathodic materials.

3.8.1. Sulphides and selenides

Many insoluble sulphide positive electrodes have been extensively studied as electrodes in secondary cells. This is most probably because of their extensive use in primary cells. The poor reversibility of these materials seemed to be because of the low solubility of the alkali and other metal sulphides in organic electrolytes [455], and because they lacked a crystal structure which would favour intercalation of lithium ions similar to TiS_2 [409].

Copper sulphide, NiS, SiS_2, MnS and FeS have been investigated [456] as cathode materials using 1M $LiAsF_6$/THF as the electrolyte.

Titanium and V give better initial performances than Cu, but the Cu is better in the long run because it is cheaper and gives better performances after 35 cycles [457]. It can deliver 1.6 and 0.98 equivalents of charge per mol of CuS at 1 mA cm^{-2} after 4 and 20 cycles, respectively. These are equivalent to 348 and 211 W h lb^{-1} if based on the weight of active material used. The main problem when using cells based on these positives is that there is a rapid drop in the capacity if electrodes having practical loadings are used. In the case of the Li/CuS system, deterioration of the lithium electrode is due to reaction of the lithium electrode with the electrolyte and a reduction of the electrolyte on the CuS electrode below ~1.5 V, which combine to limit the cycle life of the Li/CuS system.

Cyclic voltammetry experiments [458] have shown the reversibility of the Cu/CuS couple. The curves show that Cu oxidation with CuS formation occurs at a potential of about 1.03 V. One of the major difficulties encountered in using CuS as a cathode is its poor solubility in organic solvents. Macrocyclic polyethers have been added to try and enhance its solubility, but the effect has only been marginal. If DMF is used, however, addition of Lewis acids of the type BX_3 considerably increases the concentration of sulphide in the DMF. The voltage plateau of this cell on load is 1.55 V. It is unlikely that any major improvements will occur in this secondary cell until an electrolyte which is more resistant to reduction has been found so that the end point (now 1.4 V) can be increased without a further loss in the cell capacity.

The layered chalcogenides of the type MX_2 [459 - 461], for example, $NbSe_2$, TeS_2 and TiS_2, act as reversible cathodes in non-aqueous solvents. This is because the MX_2 structure behaves as an inert host structure for intercalated, electrochemically active species, *e.g.*, I_2 in Li/LiI, PC/I_2–MX_2 cells [462]. It was thought that in this cell the reaction was:

$$Li + \tfrac{1}{2}I_2(\text{in } MX_2) \rightleftharpoons LiI,$$

but it was later shown that MX_3 [463 - 465] behaves reversibly in the absence of I_2. The synthesised cathode $MX_{4.5}$ [466] is also reversible. It is now believed that the reaction of MX_y type cathodes involves topotactic intercalation of lithium into the layered MX_y structure with $M^{4+} \rightarrow M^{3+}$, and in the higher chalcogenides the cleavage of the X–X bond

$$n\text{Li} + MX_y \rightleftharpoons Li_nMX_y \text{ [409, 467, 468].}$$

The use of MX_y cathodes relies on maintaining the integral structure of the MX_y on cycling the lithium ions into (discharge) and out of (charge) the MX_y cathode material. To be good cathodes they must enable the Li/MX_2 couple to provide a sufficiently high voltage and, in general, to maintain its structure and morphology, although, in some cases — $NbSe_3$ for example — a structural change can be beneficial as it increases the plateau voltage. This is thought to be due to an initial structural change which occurs on insertion of the lithium ions into the $NbSe_3$ lattice but the nature of this reaction is unknown. $NbSe_3$ has a high conductivity, and therefore no conductive diluent is necessary. It has a cycling efficiency greater than 80% at room temperature. At higher temperatures (60 °C) in $LiAsF_6$, PC cell life is limited by anode failure.

Several other metal chalcogenides are known to be reversible with low current drains, but their performance is very poor on deep discharge.

Murphy and Trumbore [469, 470] have recently reviewed the types of MX_y cathodes used.

Crystalline compounds have been extensively used as cathode materials [450], especially the dichalcogenides. One such is TiS_2 which, having a very porous structure and only a small lattice expansion on recyling [418], is a very reversible material. Li_2VSe_2 is also reversible.

$LiVX_2/Li_2VX_2$ (X = S, Se) couples can be recharged and consist of two phases between their limiting compositions. The selenide is reversible over the range $VSe_2 \rightleftharpoons Li_2VSe_2$, but the sulphide deteriorates if it is not confined to the $LiVS_2/Li_2VS_2$ couple [471]. The dichalcogenides of Groups IVB, VB metals are the most common. The cathodic reaction is believed to be

$$Li^+ + MX_2 + e^- \rightleftharpoons LiMX_2.$$

The Li/LiClO$_4$, PC/VSe$_2$ system shows the presence of two plateaus. Each plateau is of equal capacity and is reversible. On initial cycling, the first plateau is 83% efficient but falls to 75% by the sixth cycle. The constant voltages of both plateaus suggest the presence of two phases [471] between VSe_2–$LiVSe_2$ and $LiVSe_2$–Li_2VSe_2. This was verified by X-ray analysis.

In the case of the Li/LiClO$_4$, PC/LiVS$_2$ system, there is an additional capacity of 0.95 equivalents per V atom near 1.0 V. This additional capacity decreases to 0.6 equivalents after 30 cycles. The additional capacity is most probably the result of the readily reversible $Li_2VS_2/LiVS_2$ couple. Further, charging of this couple to yield VS_2 leads to a rapid deterioration over the entire voltage range.

Replacing the vanadium with iron enhances the reversibility in $V_{(1-x)}$-$Fe_xS_2/LiV_{(1-x)}Fe_xS_2$ couples [472] but this causes the lower voltage process to be irreversible. In lithium electrochemical cells, V_2S_2 cathodes react with 2.5 lithium per vanadium above 1.4 V. On primary discharge at 0.5 mA cm^{-2}, 85% of the capacity can be recovered on the first recharge to 2.8 V also at 0.5 mA cm^{-2}. On repeated cycling, however, the capacity falls to 30% of its initial value with an accompanying change in the voltage composition profile.

Niobium selenide has also been extensively studied [473], mainly in the system Li/LiClO$_4$, PC/NbSe$_x$ where $x = 2, 3, 4, 4.5$.

$NbSe_2$ is similar to TiS_2 [409] in that no irreversible chemical changes occur. $NbSe_2$ is fully reversible *via* lithium intercalation. This is facilitated by the fact that only one phase is involved during cycling.

The higher selenides are reversible to varying degrees but the equilibrium charge voltage exceeds the initial discharge voltage by at least 15%, indicating that the cell chemistry is more complicated than initially believed. Many of the changes have been shown to occur during the first cycle.

$NbSe_3$ has a lower voltage on the initial recycle, but $NbSe_4$ and $NbSe_{4.5}$ both have higher voltages showing that, in the higher selenides, a multiphase system, or a gradual change in the structure is taking place. The discharges of $NbSe_3$ and TiS_3 are similar [468] and involve 3 lithiums per MX_3. Using the reaction with n-BuLi as a model for discharge, it has been shown that the reaction is a topochemical one in which the basic structure of the MX_3 is maintained. $NbSe_3$ and TiS_3 consist of chain structures having X–X bonds. To account for the stoichiometry, we must assume that, apart from the M^{4+} cation, the $(X_2)^{2-}$ anion groups are also reducible.

The partial reversibility of the TiS_3 cell (compared with the complete reversibility of the $NbSe_3$ cell) could be associated with the change in the coordination geometry of the Ti^{4+}, which changes from a trigonal prismatic to an octahedral arrangement.

γ-$NbSe_4$ with a single phase composition range between $NbSe_4$ and $NbSe_{4.5}$ has proved a very useful cathode material [466]. It reacts *via* a topotactic reaction to give an $Li_4NbSe_{(4-x)}$ ($x = 0 - 0.5$) discharge product [409]. The eventual cell degradation, if not due to lithium failure, is due to the cathode break-up rather than irreversibility.

Transition metal chalcogenides are now preferred to the transition metal halide salts [474]. One of those which has been extensively studied is the Li/TiS_2 combination. It has been widely used with the lithium thiocyanate electrolyte in the form:

Li/LiSCN, 3-dioxolane/1,2-DME

as it is both thermally and electrochemically stable, except for the slow formation of dioxolane oligomers.

The reversibility of TiS_2 is evidenced by the galvanostatic anodic and cathodic polarization cycles [475] which have been explored over various sweep rates and over the entire range of composition up to 1 mole of lithium per mole of dichalcogenide. The results showed complete reversibility with no hysteresis between the cathodic or anodic cycles and suggest that lithium diffusion into the lattice is the limiting step, having a comparatively slow rate of only 10^{-8} cm^2 s^{-1} [476] in TiS. The rate of the diffusion depends on the lithium concentration in the dichalcogenide. The lithium which initially diffuses into the matrix was found to be strongly bonded to the TiS_2 matrix, and was very difficult to remove. It has been suggested that the initial species may open the Van der Waals gap between the layers, promoting more intercalation of lithium and enhancing reversibility as the concentration increases. The cycling performance reaches a maximum at concentrations greater than 0.4 Li per TiS_2 mole fraction, in accordance with the polarization data [475]. The concept of 100% rechargeability is invalidated because it cannot sustain deep cycles (even in $LiAsF_6$ in 2-MeTHF [477]) due to the poor cyclability of the lithium because of the surface passivation or encapsulation.

The cycling efficiency is between 80 and 90% on the first discharge. These figures are, however, sensitive to the anode and cathode loadings, and the electrodeposition and stripping efficiencies on a copper substrate at current densities between 0.4 and 1.5 mA cm^{-2} fell from 85% to 40%. Changes in the TiS_2 utilization efficiency on the first discharge have been measured over a range of current densities to 1.4 V (*vs.* the lithium reference). A sharp drop was found to occur at 45 mA cm^{-2}. At low current densities and at low depths of discharge (less than 10%) these cells can be cycled a number of times [478]. On overdischarge and overcharge, however, solvent decomposition is a problem and, on recharge, dendritic plating of lithium is also serious. As the cell is recycled, its capacity falls due to the loss of structural integrity in the cathode and a softening of its edges. The latter could be caused by high current densities at the edges and is thus an indicator of uneven reaction. Dendrite growth may also be a serious problem with prolonged storage and deep discharge cycling.

At low current densities and at room temperature LiSCN and DME are both stable and a porous lithium anode is observed.

Titanium sulphides of the form $Ti_{(1+x)}S_2$ and TiS_2 nevertheless show good reversibility, and their discharge cycles are characterised by flat voltage plateaux at about 2.0 V *vs.* the lithium. The limiting capacities approach 1 and 3 equivalents of charge/mole of TiS_2 and TiS_3, respectively. Capacities between 0.8 and 0.4 equivalents of charge/mole of TiS_x were obtained after at least 300 100% discharges at the $C/3$ rate [451]. During the initial cycles, capacities greater than 1 equivalent of charge/mole of TiS_3 were observed. The reaction mechanism involves lithium ion intercalation into the layered structure of the sulphide. These cathodic materials have measured capacities of 360 and 180 W h kg^{-1}, respectively. Of the two, TiS_2 seems to be the best because of its greater reversibility.

3.8.2. Sulphospinels

Chalcospinels, especially the sulphospinels, have been discovered to behave as good positives which operate at room temperature through a reversible topochemical takeup of lithium, up to three electrons per mole in aprotic solvents [479, 480]. These face centred cubic materials are sulphur equivalents of oxospinels of formula M_1^{II} M_2^{III} S_4. $CuCo_2S_4$–Li and others where Ni and Fe replace the cobalt have been studied. They are high energy cathode materials which can be used both at room and at elevated temperatures, and, as they are good conductors, they are suitable cathode materials for high discharge rates.

Reversible cycling is due to interstitial migration of lithium into the face centred cubic structure. X-ray studies confirmed that the face centred cubic structure is retained when up to three lithium equivalents are introduced per mol of sulphospinel by the n-butyllithium titration.

$CuCo_2S_4$ and $CuNi_2S_4$ appear to be the best sulphospinels although it is believed that the poor qualities of the $CuFe_2S_4$ were because of its poor preparation.

It has been found that the $CuCoS_4$ [481] yields substantially more capacity per unit active weight than does TiS_2 to comparable end point voltages. Typically, for 100% depth of discharge, *i.e.*, two electrons/mole of $CuCo_2S_4$, the end point voltage is taken as 1.2 V provided that the anode is still functioning. On recharge, the end voltage is taken as being between 2.1 and 2.4 V, and the overcharge voltage as 3 V. Two solvents have been used in this system:

(i) $LiClO_4$, THF
(ii) $LiClO_4$, THF + 30% dioxolane

The latter combination yields more (109 compared with only 59 for the former) and better recycles. Capacity is limited by the lithium anode and, as dioxolane enhances the charging characteristics of the anode, its use is preferred. Thus we see how the choice of the solvent can be very important.

3.8.3. Transition metal oxides

(a) Vanadium oxides as cathode materials. Stoichiometric $VO_{2.17}$ and non-stoichiometric $VO_{2.19}$ together with V_6O_{13} have been investigated as cathode materials in cells of the type

Li/2-MeTHF, $LiAsF_6/V_6O_{13}$

The discharge characteristics of $VO_{2.17}$ at 60 °C are equivalent to those of $VO_{2.19}$ at 20 °C. The rechargeabilities of the $VO_{2.17}$ and $VO_{2.19}$ cathodes depend on the lower voltage cut-off which, in the case of these cathodes, is fairly high. This is because of the presence of a relatively high capacity irreversible process at about 1.6 V, and the cycling limits which have been set at 3 V and 1.9 V for $VO_{2.17}$ and $VO_{2.19}$, respectively. Even with these limitations, these oxides have been used in three different types of hermetically sealed cells.

Murphy *et al.* [419] have studied the rutile and perovskite-related oxides. Their results show that V_6O_{13} should be good as a high energy density cathode material. Calculations based on its reactions in n-butyllithium, in which there is an uptake of about 8 lithium atoms per mol of V_6O_{13}, give a theoretical energy density of about 850 W h kg^{-1} [419]. In practice, however, this figure is not reached, but it nevertheless still shows good secondary characteristics [483].

V_6O_{13} and its related oxides have been studied in 2-MeTHF, $LiAsF_6$ electrolytes. The first discharge of $VO_{2.19}$ resulted in a capacity of about 1 e^- per vanadium at current densities as high as 2 mA cm^{-2}. After the first overcharge, the capacity fell by between 15 and 20% (even at current densities as low as 0.1 mA cm^{-2}) and after only a few cycles, the capacity fell to 0.7 e^- per vanadium, but then remained constant.

There are two major drawbacks in the use of these oxides as cathode materials:

(i) the necessity to add graphite as a conductive diluent. This results in a low volumetric energy density which to some extent can be compensated for by adding Cr or Fe to the V^0 lattice;

(ii) the presence of a performance limiting, irreversible reduction process which occurs at potentials below 1.7 V.

Nevertheless, V_6O_{13} has proved to be a very good cathodic material. It has a very open structure and a high conductivity. The average cell voltage of the Li/V_6O_{13} couple is 2.2 V with a theoretical energy density of 800 W h kg^{-1}. The excellent rechargeability of this material [482] makes it an exceptional cathode.

V_2O_5 has also been investigated as a cathode material in the Li/1M $LiClO_4$, PC/V_2O_5 system in which the reaction may be written

$$V_2O_5 + x\mathrm{Li} \rightleftharpoons \mathrm{Li}_xV_2O_5 \ [484]$$

The reaction consists of two successive steps with x over the range 0 - 1 and 1 - 3, respectively. In the first step, structural changes that occur in the V_2O_5 lattice are reversible, but the second step is irreversible.

V_2O_5, even though it has one of the highest on load voltages [485] has therefore proved a less suitable cathode material than V_6O_{13} [486]. This is because of:-

(i) its low conductivity;

(ii) its irreversible reduction at moderate potentials;

(iii) its ability to oxidise the electrolyte. This occurs because the volumes of the unit cells are too small to allow a fast uptake of the electrolyte [482].

(b) Molybdenum oxides. The use of molybdenum oxides as cathode materials in secondary lithium cells has been extensively studied [487]. From these studies, it is clear [488, 489] that all molybdenum oxides with compositions between MoO_2 and MoO_3 reversibly incorporate lithium.

$Mo_{17}O_{47}$ has the highest capacity after several cycles. Its voltage drop on full discharge (about 1.9 V), however, is greater than for TiS_2 (0.6 V) and off-stoichiometric $V_6O_{13.2}$ (0.8 V). The average cell voltage (1.85 V) is less than $V_6O_{13.2}$ (2.2 V). Furthermore, the energy density of this material, 490 W h kg^{-1}, is less than $V_6O_{13.2}$, 800 W h kg^{-1}. Based on these considerations, $Mo_{17}O_{47}$ is not as good a cathodic material as off-stoichiometric $V_6O_{13.2}$.

Mo_4O_{11}, Mo_8O_{23} and Mo_9O_{26} have also been considered as cathodic materials [490]. They can form ternary phases from which the lithium cation can be quantitatively recovered on charge for limited e/Mo values, for example, 0.8 for Mo_8O_{23}. The higher ratios make the reduction irreversible due to the breakdown of the lattice. Of these three materials, Mo_8O_{23} has proved to be the best because it behaves reversibly with good voltage retention, even at discharge depths near the limiting values.

In the case of Mo_8O_{23}, the van der Waals gaps can easily be filled by small cations. The diameter of the lithium cations are only 0.07 nm, which makes them freely mobile in the Mo_8O_{23} lattice which has a spacing of 0.27 nm.

The limiting factor seems to be the transport of the lithium in the $LiClO_4$, PC from the anode to the cathode. This means that the lithium cations entering the cathode are not replaced fast enough by those from the anode. At 1 mA cm^{-2} and to a 2 V cut-off, 85 A h kg^{-1} (0.89 C/Mo) and 200 W h kg^{-1} were obtained, which corresponds to $Li_{7.1}Mo_8O_{23}$. Therefore, this material is better than the 3D system V_2O_5 in which we get bond cleavage [409] and, hence, the loss of total reversibility.

Mo_8O_{23} accepts 1.0 lithium cations/Mo and single charge/discharge efficiencies as high as 95% at 1 mA cm^{-2} and 0.5 *e*/Mo have been observed. The results after prolonged cycling are also good [491] as it is able to retain its charge and structure well. The anode also shows good adhesion of the active material and lack of dendrites. This cathode also has a high specific capacity and a high energy density. Mo_8O_{23}, nevertheless, shows room for improvement, as performance is clearly limited by the cathode technology.

Prototype secondary cells employing MoO_3 as the cathode material in cells of the type Li/$LiAlCl_4$, BL/MoO_3, C have also been examined [492]. In this solvent, the cathode has a low solubility, and a satisfactory polarization behaviour. The charge/discharge efficiencies approach 100%. In the above mentioned cell, which may be discharged at 0.5, 1.0, 2.0 mA cm^{-2}, there are good efficiencies if based on a two electron transfer.

Oxides of the type $Mo_xO_{(3x-1)}$ may be used but the *e*/Mo values which allow structural retention in the $Li_{my}Mo_mO_{(3m-1)}$ ternary phases are lower than in MoO_3. Nevertheless, its higher maximum efficiencies, and lack of need for a conductive diluent are such that it may be used as a cathode material.

Mo_8O_{23} is only one of a few compounds which have 3D structures which may be used as cathode materials. It also has the added benefit of being cheap.

Apart from V_2O_5, the Mo oxides have the highest on load potentials [490]. In the case of $Mo_{18}O_{52}$ [485] which has a layered structure, its good electronic properties are superior to those of V_2O_5, especially at low current densities.

3.8.4. Organic compounds

Recently, more attention has been given to organic positives in lithium secondary cells. Based on the weight of active material, the phthalocyanines are the best positives, the Li/Fe phthalocyanine system being able to supply 1440 A h kg^{-1} [493].

The Li/Cu phthalocyanine system can be recycled over 100 times at discharge depths of 157 A h kg^{-1}. The reaction is known to be by intercalation because:-

(i) the phthalocyanine reacts with the lithium. This has been shown to be the case by its reaction with n-butyllithium.

(ii) polymorphs affect the discharge capacity, which suggests that solid-state phthalocyanine reacts with the lithium ions.

(iii) X-ray analysis shows that the phthalocyanine unit cell becomes enlarged after discharge, thus indicating lithium intercalation between the molecules.

As these positives have good, rechargeable characteristics and an on load plateau of 2 V over a wide range of charge, it is likely that these materials will be further developed.

Organic cells using reversible *n*- and *p*-type electrochemical doping of polyacetylene $(CH)_x$ have also been developed [494]. The $(CH)_x$ may be doped *n* or *p* to give organic metals which can replace both conventional cathodes and the lithium anode in lightweight cells. In a *p* doped material we get incorporation of anions, *e.g.*, I_3^-, ClO_4^- or AsF_6^- to give $[CH^{y+}A_y^-]_x$ where A represents the anion [495].

$(CH)_x$ can be reversibly electrochemically doped *n* or *p* type, and the undoping of various combinations of *p* and/or *n* doped $(CH)_x$ can be utilized in secondary cells of three basic kinds:

(i) those in which the anode discharge involves $(CH)_x$ derivatives,
(ii) only the cathode involves $(CH)_x$ derivatives,
(iii) both electrodes are involved.

3.8.5. Other cathodic materials

Recently, several new cathode materials have been examined to assess their potential for use in secondary lithium cells.

One of these new materials is thiochromite. Phases of the type Na_xCrS_2 ($x > 0.1$) [496] have been prepared which provide hosts for lithium cation intercalation. In these cells, more than one equivalent of lithium cation per mole of $NaCrS_2$ can be reversibly intercalated at high rates. Furthermore, the 3D structure proves sufficiently rugged to allow repeated cycling with only minor losses in capacity. The Li/Na_xCrS_2 couple has a high theoretical energy density of 518 W h kg^{-1} and, even when based on a discharge of 1 mA cm^{-2} and on the real cell weight, we still get 142 W h kg^{-1} for an eight hour discharge rate. The values of the lithium cation chemical potential in Na_xCrS_2 and of the free energy of intercalation have both large negative values which are typical of efficient chalcogenide cathode materials.

Lead compounds have also been investigated as positives in lithium cells [497] and PbF_2, $PbCrO_4$ and PbO_2 have all been used. These compounds form intermetallics which explain the higher specific energy than those expected from the formation of Pb^0. The following intermetallics are all formed: LiPb [498], Li_5Pb_2, Li_3Pb, $Li_{10}Pb_3$, and Li_4Pb, but of these, it is the LiPb which is the most important.

3.9. Choice of materials for cell construction

These have to be corrosion resistant: one of the most important factors governing cell construction is the anodic stability of Ni, Ti, Ta or cold rolled steel (CRS). They have been studied in 1M $LiAsF_6$, THF and voltammetry showed that they were all stable in the range from 2 to 4.2 V *vs.* the Li/Li^+. In the case of Ti, however, polymerisation of the electrolyte occurs. In both Ni and CRS, corrosion was virtually zero below 4.2 V but, at 4.4 V, rapid pitting of the CRS occurred in under three hours [478]. As a result of these investigations, the best combination was found to be that of Ni plated onto CRS.

Previously, when the electrolyte was only THF, the maximum charging voltage was 3.5 V, but using $LiAsF_6$, THF, it can be as high as 4.2 V.

3.10. Conclusions

It is clear that from the present survey, we are able to conclude that in spite of much research, a great deal of work has to be done in order to bring the efficiency and ease of operation of lithium secondary cells up to that of the lithium primary cells. The best published performances obtained to the authors' present knowledge are:

(i) a charge of about 50 C mg cm^{-2};

(ii) a lithium loss of about 7.5 mg cm^{-2};

(iii) about 70 cycles if the lithium concentration is increased ten-fold.

It is our opinion that if the lithium secondary cell is to become a reality then improvements will have to be made to both the electrolyte and the anode preparation. Specifically:

(a) more inert electrolytes will have to be developed, or those which can "recontact" isolated dendrites or redissolve them (self-discharge);

(b) more attention must be paid to anode preparation and the development of improved Li/Al combinations which are better understood.

List of symbols

W h/kg	Energy density
W h/lb	Energy density
A h/g	Specific capacity
$C/3$	Discharge
C	Coulombs
V	Volts
u	Electric tension of a galvanic cell or an electrode (electrode potential following Stockholm Conv.)
I	Current density
$\Omega^{-1}\ \text{cm}^{-1}$	Conductivity
t^+	Transport number of Li^+ cation
z	Charges on ions
r	Ionic radii
η	Overvoltage
a	Constant in Tafel equation
b	Constant in Tafel equation
DMSO	Dimethyl sulphoxide
PC	Propylene carbonate
NM	Nitromethane
BL	γ-butyrolactone
DMF	Dimethylformamide
IPA	Isopropylamine
MA	Methyl acetate
THF	Tetrahydrofuran
PVP	Poly(vinylpyridine)
DME	Dimethoxyethane

MF	Methyl formate
THP	Tetrahydropyran
DEE	Diethyl ether
BHT	Butylated hydroxytoluene
PDA	Pyromellitic dianhydride: 1,2,4,5-benzenetetracarboxylic acid dianhydride
F.C.C.	Face centred cubic
Å	Ångstroms
E.L.T.	Emergency landing transmitters

References

1 J. P. Harivel, High Energy Combinations, in Performance Forecast of Selected Static Energy Conversion Devices, *Agard Propulsion and Energetics Panel, 1967.*

2 A. N. Dey, *Thin Solid Films, 43* (1977) 131.

3 J. O. Besenhard and G. Eichinger, *J. Electroanal. Chem., 68* (1976) 1.

4 A. Brenner, *J. Electrochem. Soc., 118* (1971) 99.

5 R. Dotzer, *Chem. Ing. Tech., 36* (1964) 616.

6 F. H. Hurley and T. P. Wier, Jr., *J. Electrochem. Soc., 98* (1951) 203.

7 L. Fischer, G. Winkler and G. Jander, *Z. Elektrochem., 62* (1958) 1.

8 J. O. Besenhard and G. Eichinger, *J. Electroanal. Chem., 70* (1976) 1.

9 J. N. Butler, D. R. Cogley and J. C. Synott, *J. Phys. Chem., 73* (1969) 1.

10 R. F. Scatt, *J. Electrochem. Soc., 117* (1970) 295.

11 G. W. Jackson and G. E. Blomgren, *J. Electrochem. Soc., 116* (1969) 1483.

12 J. Jorne and Ch. W. Tobias, *J. Electrochem. Soc., 121* (1974) 994.

13 S. G. Meibuhr, *J. Electrochem. Soc., 117* (1970) 56.

14 S. G. Meibuhr, *J. Electrochem. Soc., 118* (1971) 1320.

15 G. J. Janz and R. P. Tomkins, *Nonaqueous Electrolyte Handbook,* Vol. 1, Academic Press, New York, 1972.

16 J. P. Hoate and C. R. Wiese, *J. Electrochem. Soc., 121* (1974) 83.

17 J. P. Gabano, Y. Jumel and J. F. Laurent, in D. H. Collins (ed.), *Power Sources 2,* Pergamon Press, Oxford, 1970, p. 255.

18 J. M. Butler, *J. Electroanal. Chem. Interfacial Electrochem., 14* (1967) 89.

19 W. F. Meyers and S. G. Abens, Development of High Energy Density Primary Batteries, *Second Quarterly Rep., Contract NAS 3-6004 (Dec. 1964), NASA CR54307.*

20 D. P. Boden, H. R. Buhner and V. V. Spera, High Energy Battery System — Organic Electrolyte, *1st Quarterly Rep., Contract DA 28-043-AMC-0134.* Oct. 6, 1965.

21 W. Elliott, S. Hsu and W. Towle, *Final Rep., Contract NAS3-2790,* July, 1964.

22 J. C. Cessna, *Corrosion, 27* (1971) 244.

23 R. Jasinski and S. Carroll, *J. Electrochem. Soc., 117* (1970) 218.

24 S. G. Meibuhr, *J. Electrochem. Soc., 117* (1970) 56.

25 Y. Takada, Y. Miyake (Govt. Ind. Res. Inst., Osaka, Japan) *Osaka Kogyo Gijutsu Shikensho Kiho, 30* (1979) 1, 27 - 31.

26 W. S. Harris, Electrochemical studies in cyclic esters, *Thesis,* UCRL-8381, July, 1958.

27 B. Burrows and R. Jasinski, *J. Electrochem. Soc., 115* (1968) 365.

28 F. P. Douser, *J. Electroanal. Chem. Interfacial Electrochem., 46* (1973) 281.

29 Ethylene carbonate, *Tech. Bull.,* Jefferson Chemical Co., Houston, Texas.

30 Propylene carbonate, *Tech. Bull.,* Jefferson Chemical Co., Houston, Texas, 1960.

31 *Rep. AD-768-500,* 1973, Batteries, Defense Documentation Center, Alexandria, VA.

32 R. Jasinski, *High Energy Batteries,* Plenum Press, New York, 1968.

33 R. Jasinski, *Electrochem. Technol., 6* (1968) 28.

34 M. L. B. Rao and K. R. Hill, *Tech. Rep., Contract No. DA-44-009-AMC-1537(T),* Sept. 1, 1966.

35 R. Selian, *Proc. 18th Annu. Power Sources Conf.*, PSC Publication Comm., Red Bank, NJ, 1964, p. 86.

36 H. Bauman, *Proc. 18th Annu. Power Sources Conf.*, PSC Publication Comm., Red Bank, NJ, 1964, p. 89.

37 J. Farrar, R. Keller and C. Mazac, *Proc. 18th Annu. Power Sources Conf.*, PSC Publication Comm., Red Bank, NJ, 1964, p. 92.

38 M. Eisenberg, *Abstract No. 47,* paper presented at Electrochem. Soc. Meeting, Washington, D.C., Oct., 1964.

39 J. Farrar, R. Keller and C. Mazac, High Energy Battery System Study, *Rep. No. 4, Contract DA-36-039-AMC-03201(E),* June, 1964, *AD 450559.*

40 W. Meyers, *Final Rep., Contract NAS3-2775,* Nov., 1964.

41 R. Jasinski, *Collect. Czech. Chem. Commun., 36* (1971) 1079.

42 K. H. M. Braeuer and J. A. Harvey, *Rep. AD 654813,* 1967.

43 H. F. Baumann, J. E. Chilton, W. J. Connor and G. M. Cook, *Rep. AD 425876,* 1963.

44 J. O. Besenhard and H. P. Fritz, *J. Electroanal. Chem., 53* (1974) 329.

45 *Ger. Auslege. 2 150 401.*

46 N. M. Nicholson and M. L. Iverson, *Ext. Abstr., 140th Meeting Electrochem. Soc., Cleveland, 1971,* p. 115.

47 G. Dalin, H. Sulkes and Z. Strachurski, *Proc. 18th Annu. Power Sources Conf.*, PSC Publications Comm., Red Bank, NJ, 1964, p. 54.

48 J. L. Weininger and F. W. Secor, *J. Electrochem. Soc., 121* (1974) 315.

49 *Ger. Offen., 2 363 777.*

50 *Ger. Offen. 2 365 044.*

51 *Ger. Offen. 2 362 587.*

52 *Ger. Auslege. 2 126 055.*

53 *Ger. Offen. 2 209 086.*

54 J. Chilton, New Cathode–Anode Couples, *Rep. No. ASD-TDR-62-1, April, 1962, (AD 277171).*

55 B. Burrows, *J. Electrochem. Soc., 118* (1971) 1130.

56 D. Herbert, *US Pat. 3,043,896,* July 1962.

57 W. Elliott, R. W. Adler, J. R. Huff, J. L. Gower and W. L. Towle, *10th Quarterly Rep., Contract NAS 3-6015,* Dec., 1966.

58 D. P. Boden, H. Buhner and V. Spera, *Final Rep., Contract DA 28-043-AMC-01344 (E),* June, 1964.

59 M. L. B. Rao and R. W. Holmes, *Electrochem. Technol., 6* (1968) 105.

60 H. Bauman, Lithium Anode Limited Cycle Secondary Battery, *Rep. No. 3, Contract AF 33(657)11709, March 1964 (AD 433543).*

61 Research and Development of a High Capacity, Non-aqueous Secondary Battery, *Rep. No. 4, Contract NAS 3-2780(1964)(N 64-30863).*

62 P. R. Mallory and Co., *Rep. No. 1, Contract NAS 3-6017,* April, 1965.

63 A. Lyall and H. Seiger, Lithium–Nickel Halide Secondary Battery, *Rep. No. 1, Contract AF 33(615)-1266, March 1964, (AD 433616).*

64 A. Lyall and H. Seiger, *Rep. No. 3, Contract AF 33(615)-1266, September 1964, (AD 605754).*

65 A. Lyall and H. Seiger, *Rep. AFAPL-TR-65-11, January, 1965, (N65-20555).*

66 G. W. Jackson and G. E. Blomgren, *J. Electrochem. Soc., 116* (1969) 1483.

67 J. Chilton, W. Conner and R. Holsinger, *Rep. No. 2, July, 1964, (AD 450428).*

68 C. L. Liotta, *J. Am. Chem. Soc., 96* (1974) 2250.

69 J. Dale, *Acta Chem. Scand., 26* (1972) 1417.

70 N. R. Young and A. O. McDougall, in J. Thompson (ed.), *Power Sources 8,* Academic Press, London, 1981, p. 91.

71 J. N. Butler, *Anal. Chem., 39* (1969) 1799.

72 R. Alexander, E. C. F. Ko, Y. C. Mac and A. J. Parker, *J. Am. Chem. Soc.*, *89* (1967) 3703.
73 M. Breant, G. Buisson, M. Porteix, J. L. Sue and J. P. Terrat, *J. Electroanal. Chem.*, *24* (1970) 409.
74 D. C. Luehrs, R. T. Iwamoto and J. Kleinberg, *Inorg. Chem.*, *5* (1966) 201.
75 G. Eichinger and H. P. Fritz, *Z. Naturforsch.*, *28b* (1973) 763.
76 G. Eichinger, *Thesis*, Tech. Univ., Munich, 1972.
77 J. C. Bardin, *J. Electroanal. Chem.*, *28* (1970) 157.
78 F. W. Dampier, *J. Electrochem. Soc.*, *121* (1974) 656.
79 A. N. Dey and M. L. B. Rao, *Rep.*, *AD 825241*, 1967.
80 F. W. Dampier and K. S. Spiegler, *Rep.*, *AD 859386*, 1969.
81 F. W. Dampier and K. S. Spiegler, *Rep.*, *AD 882890*, 1971.
82 A. N. Dey and M. L. B. Rao, in D. H. Collins (ed.), *Power Sources 2*, Pergamon Press, Oxford, 1970, p. 231.
83 S. Lerner and H. N. Seiger, *J. Electrochem. Soc.*, *117* (1970) 574.
84 M. Nicholson, *J. Electrochem Soc.*, *118* (1971) 1047.
85 J. S. Prener and J. D. Kingsley, *J. Chem. Phys.*, *38* (1963) 667.
86 M. Shaw and D. H. McClelland, *US Pat. 3393092*, July 16, 1968.
87 M. Shaw and R. Chand, *Proc. Power Sources Conf.*, *23* (1969) 76.
88 P. Fiordiponti, S. Panero, G. Pistoia and C. Temperoni, *J. Electrochem. Soc.*, *125* (1978) 511.
89 *Ger. Offen. 1 935 941.*
90 *US Pat. 3 532 543.*
91 *Ger. Auslege. 1 671 834.*
92 L. A. Rotinyan, S. V. Shishkina and K. J. Tikhonov, *Electrokhimiya*, *10* (1974) 662.
93 *Fr. Pat. 1 456 556.*
94 H. Lauck, *C.I.T.C.E., 20th Meeting, Strasbourg, 1969.*
95 *US Pat. 3 413 154.*
96 J. Weber and T. Loucka, in D. H. Collins (ed.), *Power Sources 3*, Oriel Press, Newcastle upon Tyne, 1971, p. 458.
97 *US Pat. 3 428 265.*
98 F. Seel and H. J. Guttler, *Angew. Chem.*, *85* (1973) 416.
99 M. V. Merritt and D. T. Sawyer, *Inorg. Chem.*, *9* (1970) 211.
100 W. Eiggenbach, *J. Inorg. Nucl. Chem.*, *30* (1968) 3189.
101 R. D. Rauch, K. M. Abraham, G. F. Pearson, J. K. Surprenant and B. Brummer, *J. Electrochem. Soc.*, *126* (1979) 523.
102 G. L. Holleck and J. R. Driscoll, *Electrochim. Acta*, *22* (1977) 647.
103 G. Lehmann, G. Gerbier, A. Brych and J. P. Gabano, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 695.
104 R. Hornig, *Proc. 10th I.E.C.E.C., Newark, 1975*, p. 424.
105 L. Campanella and G. Pistoia, *J. Electrochem. Soc.*, *118* (1971) 1905.
106 B. Di Pietro, V. Filippeschi, M. Lazzari, G. Pistoia and B. Scrosati, in J. Thompson (ed.), *Power Sources 7*, Academic Press, London, 1977.
107 *US Pat. 3655,585* (1972), *3947,289* (1976) to A. N. Dey and B. P. Sullivan.
108 *Ger. Offen. 2 155 890* to A. N. Dey.
109 A. N. Dey, *Ext. Abstr. No. 54, Electrochemical Society Fall Meeting, 1973.*
110 *US Pat. 3423 242* (1969) to W. F. Meyers, B. Bell and J. W. Simmons.
111 M. Lang, J. R. Backland and E. C. Weidner, *Proc. 26th Power Sources Symp., Atlantic City, NJ, 1974*, PSC Publication Comm., Red Bank, NJ, p. 37.
112 A. A. Inocencio, *J. Electrochem. Soc.*, *124* (1977) 1729.
113 A. R. Knapp, *Tech. Rep.*, *Ecom-2632*, Oct. 1965.
114 L. Campanella and G. Pistoia, *Electrochem. Soc. Meeting, Miami Beach, Florida, Oct. 8 - 13, 1972.*
115 A. N. Dey, *US Pat. 3681143* (1972).

116 F. W. Dampier, *Paper 4, Electrochem. Soc. Meeting, Miami Beach, Florida, Oct. 8 - 13, 1972.*

117 L. F. Athearn and L. C. Liang, *US Pat. 3726716* (1973).

118 L. Campanella and G. Pistoia, *J. Electrochem. Soc., 120* (1973) 383.

119 A. N. Dey, *Paper 54, Electrochem. Soc. Meeting, Boston, Mass., Oct. 7 - 11, 1973.*

120 Société des Accumulateurs Fixes et de Traction (S.A.F.T.) *French Patent 1,579,466* (July 21st, 1969).

121 L. Campanella and G. Pistoia, *J. Electrochem. Soc., 118* (1971) 1905.

122 N. Marfalit, *J. Electrochem. Soc., 121* (1974) 1460.

123 J. Farrar, R. Keller and C. J. Mazac, *Proc. 18th Power Sources Conf.*, PSC Publication Comm., Red Bank, NJ, 1964, p. 92.

124 T. Ohzuku, Z. Takehara and S. Yoshizawa, *Electrochim. Acta, 24* (1979) 219.

125 *US Pat. 3681144.*

126 F. M. Kimmerle and G. Giasson *J. Electrochem. Soc., 120* (1973) 1214.

127 *US Pat. 3542 601* (1970) to J. P. Gabano.

128 *US Pat. 3511 716* (1970) to J. P. Gabano.

129 J. P. Gabano, V. Dechenaux, G. Gerbier and J. Jammet, *J. Electrochem. Soc., 119* (1972) 459.

130 J. P. Gabano, G. Gerbier and J. F. Laurent, *Proc. 23rd Power Sources Symp., Atlantic City, NJ., 1969,* PSC Publication Comm., Red Bank, NJ, p. 10.

131 *Ger. Offen., 2117 114.*

132 *Ger. Offen. 2117 109.*

133 G. Lehmann, G. Gerbier, A. Brych and J. P. Gabano, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975.

134 *Data sheets of Dupont Electrochemical System,* Dupont.

135 A. J. Jacobson, M. Stanley Whittingham and Suzanne M. Rich, *J. Electrochem. Soc., 126* (1979) 887.

136 M. S. Whittingham and A. J. Jacobson, *J. Electrochem Soc., 128* (1981) 485.

137 D. W. Murphy and F. A. Trubore, *J. Electrochem. Soc., 123* (1976) 960.

138 B. Di Pietro and B. Scrosati, *J. Electrochem. Soc., 126* (1979) 729.

139 A. N. Dey, *Thin Solid Films, 43* (1977) 131.

140 *US Pat. 3736 184.*

141 *US Pat. 3711 334.*

142 *US Pat. 3658 592.*

143 *Ger. Offen. 2153 362.*

144 G. Lehmann, T. Rassinoux, G. Gerbier and J. P. Gabano, in D. H. Collins (ed.), *Power Sources 4,* Oriel Press, Newcastle upon Tyne, 1973, p. 493.

145 *Ger. Offen. 2154 092.*

146 *Ger. Offen. 2505 062.*

147 J. P. Gabano, personal communication to N. Marincic in *J. Appl. Electrochem., 6* (1976) 468.

148 F. Bonino, C. Forte, M. Lazzari and B. Scrosati, *J. Power Sources, 3* (1978/1979) 257.

149 B. Scrosati, B. Di Pietro and M. Lazzari, *J. Appl. Electrochem., 8* (1978) 369.

150 F. Bonino, M. Lazzari and B. Scrosati, *J. Electroanal. Chem. Interfacial Electrochem., 93* (1978) 117.

151 S. Conte, V. Filippeschi and G. Pistoia, *J. Power Sources, 1* (1977) 2.

152 F. Bonino and M. Lazzari, *J. Electroanal. Chem. Interfacial Electrochem., 93* (1978) 117.

153 B. Di Pietro and B. Scrosati, *J. Electrochem. Soc., 126* (1979) 729.

154 G. Lehmann, T. Rassinoux, G. Gerbier and J. P. Gabano, in D. H. Collins (ed.), *Power Sources 4,* Oriel Press, Newcastle upon Tyne, 1973.

155 R. T. Foley, J. S. Swinehart and L. Schubert, *Rep., N-65278315196,* American Univ., Washington D.C.

156 O. Paez, E. T. Seo and H. P. Silverman, *Rep., AD 655 271,* 1967, T.R.W. Systems, Redondo Beach, CA.

157 R. F. Fogle, E. T. Seo and H. P. Silverman, *Rep. AD 668 936*, 1967, T.R.W. Systems, Redondo Beach, CA.
158 *US Pat. 3073 844.*
159 D. N. Benninon, M. J. Schaer and W. C. Spindler, *Rep., AD 658 111*, 1967, Naval Ordanance Lab., Corona, CA.
160 A. A. Inocencio, *J. Electrochem. Soc., 124* (1977) 1729.
161 *US Pat. 3073844.*
162 B. A. Gruber, *Proc. 18th Power Sources Conf.*, PSC Publication Comm., Red Bank, NJ, 1964, p. 94.
163 A. A. Inocencio, *J. Electrochem. Soc., 124* (1977) 1729.
164 J. J. Auborn, K. French, A. Heller, S. Liebermann and V. Shah, *Rep., AD 746633*, 1972, G.T.E. Labs. Inc., Bay Side, NY.
165 *Ger. Offen. 2262 256.*
166 *Ger. Offen. 2263 115.*
167 J. J. Auborn, A. Heller and K. W. French, *Proc. 25th Power Sources Symp.*, PSC Publication Comm., Red Bank, NJ, 1972, p. 6.
168 *Fr. Pat. 2079744.*
169 J. J. Auborn, K. French and A. Heller, *Rep., AD 741 351*, 1972, G.T.E. Labs. Inc., Bay Side, NY.
170 D. R. Cogley and M. J. Turchan, *Rep., AD 779 477*, 1974, E.I.C. Inc., Newton, MA.
171 J. J. Auborn, K. W. French and A. Heller, in *Proc. Symp. Corrosion Problems in Energy Conversion and Generation, New York, 1974*, p. 56.
172 Mallory (P.R.) and Co. Inc., *Rep., AD/A 006 647*, 1974, Mallory P.R. and Co. Inc., Burlington, MA.
173 N. Marincic and A. Lombardi, *Rep., AD/A 006 810*, 1975, G.T.E. Labs. Inc., Waltham, MA.
174 N. Marincic and A. Lombardi, *Rep., AD/A 012 093*, 1975, G.T.E. Labs. Inc., Waltham, MA.
175 J. J. Auborn, K. W. French, S. I. Liebermann, V. K. Shah and A. Heller, *J. Electrochem. Soc., 120* (1973) 1613.
176 J. J. Auborn, K. W. French, S. I. Liebermann, V. K. Shah and A. Heller, *Rep., AD 763 478*, 1973.
177 W. K. Behl, J. A. Chrisrophocus, M. Ramirez and S. Gilman, *J. Electrochem. Soc., 120* (1973) 1619.
178 A. N. Dey, *Thin Solid Films, 43* (1977) 131.
179 *US Pat. 3536-532* (1970) to N. Watanabe and M. Fukuda.
180 M. Fukuda and T. Iijima, *Ext. Abstr. No. 41, Electrochemical Society Fall Meeting, 1971.*
181 M. Fukuda and T. Iijima, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 713.
182 M. Fukuda and T. Iijima, *I.E.C.E.C. 74 Record*, 1975, p. 413.
183 *Ger. Pat. 1917907.*
184 *US Pat. 3536 532.*
185 *Ger. Offen. 2344 748.*
186 M. Fukuda and T. Iijima, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 713.
187 R. G. Gunther, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 729.
188 P. Fiordiponti, S. Panero, G. Pistoia and C. Temperoni, *J. Electrochem. Soc., 125* (1978) 511.
189 G. Jander, *Die Chemie (1949) in Wasserahwlichen Losungsmittein*, Springer, Berlin.
190 S. C. Lévy, *SAND-75-0646*, March 1977, Sandia Labs., Albuquerque, NM.
191 R. Holmes, N. Marincic and H. Taylor, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 703.
192 Meyers and Simmons, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 703.

193 D. Linden and B. McDonald, *J. Power Sources 5*, (1980) 35.
194 R. Holmes, N. Marincic and H. Taylor, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 703.
195 P. Bro, H. Y. Kang, C. Schlaikjer and H. Taylor, *I.E.C.E.C. 75 Record*, 1975, p. 432.
196 Test Data from US Army Electronics R. and D. Command, Fort Monmouth, New Jersey, 1979.
197 B. Tuvnes, Field tests with Li/SO_2 batteries, *Proc. 28th Power Sources Symp.*, 1978, The Electrochemical Society, Princeton, NJ.
198 H. Taylor, *Proc. 12th I.E.C.E.C., 1* (1979) 288.
199 P. M. Shah, *Proc. 27th Power Sources Symp.*, PSC Publication Comm., Red Bank, NJ, 1976, p. 59.
200 H. Taylor, *TR-76-9*, P. R. Mallory and Co. Inc., Burlington, MA 01803, 1976.
201 P. Bro, R. Holmes, N. Marincic and H. Taylor, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London and New York, 1975, p. 703.
202 M. G. Rosansky and R. M. Teoeschi, *TR-0042-Q-0, TR-0042-Q-01*, Power Conversion, Inc. South. Mt. Vernon, N.Y. 10550, 1976.
203 T. Watson, *TR-0042-Q-03*, Power Conversion, Inc. South. Mt. Vernon, N.Y. 10550, 1977.
204 E. D. Wilmar, in D. H. Collins (ed.), *Power Sources, 6*, Academic Press, N.Y., 1977, p. 469.
205 A. Gilmour, Paper No. 2, Session No. 2, *ERA 78-22 Seminar*, London, 1978.
206 E. S. Brooks, *Proc. 26th Power Sources Symp.*, PSC Publication Comm., Red Bank, NJ, 1974, p. 31.
207 H. Taylor, The storability of Li/SO_2 cells, *Proc. 12th Intersoc. Energy Conversion Eng. Conf., 1977*, American Nuclear Society, La Grange Park, 111, p. 288.
208 D. Linden and B. McDonald, *J. Power Sources, 5* (1980) 35.
209 J. P. Harivel, in *Performance Forecast of Selected Static Energy Conversion Devices*, Agard Propulsion and Energetics Panel, 1967.
210 D. P. Boden, *Proc. 20th Annu. Power Sources Conf.*, PSC Publication Comm., Red Bank, NJ, 1966, p. 63.
211 M. Eisenberg and J. Pavlovic, *Final Rep., Contract No. W63-0618-C*, May, 1965.
212 C. Wolfenbuetel, *Ger. Pat. 1170659*, (May, 1964).
213 N. Sidgwick, *Chemical Elements*, Oxford Univ. Press, New York, 1950, p. 101.
214 H. Liebig, *Chem. Z., 95* (1971) 301.
215 R. Nelson and R. Adams, *J. Electroanal. Chem., 13* (1967) 184.
216 R. Meredith and C. Tobias, *J. Electrochem. Soc., 108* (1961) 286.
217 L. Marcoux and K. Prater, B. Prater and R. Adams, *Anal. Chem., 37* (1965) 1446.
218 P. Kronck and R. Fuoss, *J. Am. Chem. Soc., 77* (1955) 6114.
219 L. Chow and R. Fuoss, *J. Am. Chem. Soc., 80* (1958) 1095.
220 R. Fuoss and E. Hirsch, *J. Am. Chem. Soc., 82* (1960) 1013.
221 B. Burrows and R. Jasinski, *J. Electrochem. Soc., 115* (1968) 365.
222 J. N. Butler, in P. Delahay (ed.), *Advances in Electrochemistry and Electrochemica Engineering*, Vol. 7, Interscience, New York, 1970, p. 77.
223 R. F. Scatt, *J. Electrochem. Soc., 117* (1970) 295.
224 W. S. Harris, Electrochemical studies in cyclic esters, *Thesis*, UCRL-8381, July, 1958
225 Ethylene carbonate, *Tech. Bull.*, Jefferson Chemical Co., Houston, Texas, 1960.
226 Propylene carbonate, *Tech. Bull.*, Jefferson Chemical Co., Houston, Texas, 1960.
227 W. J. Rappel, *Ind. Eng. Chem., 50* (5) (1958) 767.
228 A. N. Dey, *Ext. Abstr. No. 62, The Electrochemical Society Meeting, Atlantic City NY, 1970.*
229 A. N. Dey and P. B. Sullivan, *J. Electrochem. Soc., 117* (1970) 222.
230 J. Jansta, F. P. Dousek and J. Riha, *J. Electroanal. Chem., 44* (1973) 263.
231 J. Courtot-Couper and M. L'Her, *Bull. Soc. Chim. Fr.*, (1970) 1631.
232 F. P. Dousek, J. Jansta and J. Riha, *J. Electroanal. Chem., 46* (1973) 281.
233 R. Keller, J. N. Foster, D. C. Hanson, J. F. Hon and J. S. Huirhead, *Contract No NAS 3-8521*, Dec. 1968.

234 W. J. Peppel, *Ind. Eng. Chem.*, *50* (S) (1958) 767.

235 J. S. Dunnett and R. P. H. Gasser, *Trans. Faraday Soc.*, *61* (1965) 922.

236 J. Lindbert, J. Kenttamaa and A. Nissma, *Suom. Kemistil.*, *34B* (1961) 156.

237 A. Ledwith and N. McFarlane, *Proc. Chem. Soc.*, (1964) 108.

238 D. E. O'Connor and W. I. Lyness, *J. Org. Chem.*, *30* (1965) 1620.

239 H. F. Bauman, J. E. Chilton and R. Mauri, Lithium Anode Limited Cycle Battery Investigations, *Tech. Rep. AFAPL-TR-66-35*, April, 1966.

240 J. N. Butler, *J. Electroanal. Chem.*, *14* (1967) 89.

241 F. P. Dousek, *J. Electroanal. Chem. Interfacial Electrochem.*, *46* (1973) 281.

242 J. N. Butler, in P. Delahay and Ch. W. Tobias (eds.), *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 7, Interscience, New York, 1970.

243 R. G. Selim, K. R. Hill and M. L. B. Rao, *1st Quarterly Rep.*, *N65-18935*, 1964.

244 W. Elliott, S-Liang Hsu and W. L. Towle, *Rep. No. 3, Contract NAS3-3790*, April, 1964, Globe Union Inc., Milwaukee, WI.

245 E. Buncel and E. A. Symons, *Chem. Commun.*, (1970) 164.

246 DMF Product Information Bulletin, Du Pont, Wilmington, Del.

247 *Netherlands Appl. 6611703*, April 24, 1967.

248 G. J. Janz and R. P. T. Tompkins, *Nonaqueous Electrolytes Handbook*, Vol. 1, Academic Press, New York, 1972.

249 A. B. Thomas and E. G. Rochow, *J. Am. Chem. Soc.*, *79* (1957) 1843.

250 B. Brummer, *J. Chem. Phys.*, *42* (1965) 1636.

251 J. E. Prue and P. J. Sherrington, *Trans. Faraday Soc.*, *57* (1961) 1795.

252 R. Jasinski and S. Kirkland, *Anal. Chem.*, *39* (1967) 1663.

253 *US Pat. 3511716.*

254 *Ger. Auslege. 1771705.*

255 A. Caillee and G. Demange-Guérin, *J. Electroanal. Chem.*, *40* (1972) 69.

256 *Ger. Offen. 2 205 099.*

257 *US Pat. 3544 385.*

258 W. E. Elliott, Shih-Liang Hsu and W. L. Towle, *Rep. No. N 65-11518*, 1964, Globe Union Inc., Milwaukee, WI.

259 G. Pistoia, M. de Rossi and B. Scrosati, *J. Electrochem. Soc.*, *117* (1970) 500.

260 *US Pat. 3 508 966.*

261 *Fr. Pat. 1527,783.*

262 *Ger. Auslege. 1 671 192.*

263 *US Pat. 3468 716.*

264 *Fr. Pat. 1516 899.*

265 *US Pat. 3660 162.*

266 J. O. Besenhard, *Thesis*, Tech. Univ. Munich, NYIS N74-30505, 1973.

267 W. Elliott, J. Huff, R. Adler and W. Towle, *Proc. 18th Annu. Power Sources Conf.*, PSC Publication Comm., Red Bank, NJ, 1964, p. 82.

268 K. Starke, *J. Inorg. Nucl. Chem.*, *11* (1959) 77.

269 P. Arthur, W. M. Haynes and L. P. Varga, *Anal. Chem.*, *38* (1966) 1630.

270 G. M. Cook, *J. Electrochem. Soc.*, *117* (1970) 559.

271 J. Jansta, F. P. Dousek and J. Riha, *J. Electroanal. Chem.*, *38* (1972) 445.

272 T. V. Rebagay, J. F. Castell and P. G. Seers, *J. Electrochem. Soc.*, *121* (1974) 977.

273 A. K. Mishra and K. N. Tandon, *J. Electrochem. Soc.*, *121* (1974) 910.

274 J. J. Auborn and N. Marincic, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 683.

275 D. Linden, N. Willburn and E. Brooks, in D. H. Collins (ed.), *Power Sources 4*, Oriel Press, Newcastle upon Tyne, 1973, p. 483.

276 N. T. Wilburn, *25th Power Sources Symp.*, PSC Publication Comm., Red Bank, NJ, 1972, p. 3.

277 *US Pat. 3663 721.*

278 N. R. Young and A. D. McDougall, in J. Thompson (ed.), *Power Sources 8*, Academic Press, London, 1981, p. 91.

279 J. Cooper and A. Fleischer (eds.), Battery separator screening methods, *AD 447301*, Air Force Aero Propulsion Lab., Wright-Patterson AFB, 1964.
280 G. W. Jackson and G. E. Blomgren, *J. Electrochem. Soc., 116* (1969) 1483.
281 W. S. Harris, *Thesis*, Univ. California, Berkely, 1958.
282 A. A. Inocencio, *J. Electrochem. Soc., 124* (1977) 1729.
283 W. P. Kilroy and C. T. Moynihan, *J. Electrochem. Soc., 125* (1978) 520.
284 D. R. Flinn and K. N. Stern, *J. Electrochem. Soc., 123* (1976) 978.
285 R. T. Johnson, Jr., R. M. Biefeld, M. L. Knotek and B. Morosin, *J. Electrochem. Soc., 123* (1976) 680.
286 I. D. Raistrick, L. Ho and R. A. Huggins, *J. Electrochem. Soc., 123* (1976) 1469.
287 G. C. Farrington, *J. Electrochem. Soc., 123* (1976) 591.
288 R. Jasinski, in P. Delahay and Ch. W. Tobias (eds.), *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 8, Interscience, New York, 1971.
289 R. G. Selim, K. R. Hill and M. L. B. Rao, *Rep. N-6635218*, 1965, Mallory P.R. and Co. Inc., Burlington, MA.
290 R. Jasinski and S. Carroll, *J. Electrochem. Soc., 117* (1970) 218.
291 J. N. Butler, D. R. Cogley and J. C. Synott, *J. Phys. Chem., 73* (1969) 4026.
292 R. F. Scarr, *J. Electrochem. Soc., 117* (1970) 295.
293 S. Anderson, Anderson Physics Lab., Champagne IL, in *Electrochem. Technol., 6* (1968) 35.
294 A. N. Dey, *Ext. Abstr. No. 62, Electrochemical Society Fall Meeting, 1970*, Electrochemical Society, Princeton, N.J.
295 R. Jasinski and S. Carroll, *J. Electrochem. Soc., 117* (1970) 218.
296 A. N. Dey, *Ext. Abstr. No. 62, Electrochemical Society Meeting, Atlantic City, NY, 1970.*
297 R. C. Shair, A. E. Lyall and H. N. Seiger, in D. H. Collins (ed.), *Power Sources 2*, Pergamon Press, Oxford, 1970, p. 267.
298 J. Chilton, W. J. Conner and R. W. Holsinger, *Rep. No. 3, Contract AF 33 (615)-1195*, October, 1964, *(AD 607968)*, Lockheed Missiles and Space Co., Sunnyvale, CA.
299 R. F. Scarr, *J. Electrochem. Soc., 117* (1970) 295.
300 S. G. Meibur, *J. Electrochem. Soc., 117* (1970) 56.
301 *US Pat. 3947 289* (1976) to A. N. Dey.
302 A. N. Dey, *Ext. Abstr. No. 62, Electrochemical Society Fall Meeting, 1970*, Electrochemical Society, Princeton, N.J.
303 J. P. Gabano, G. Gerbier and J. F. Laurent, *Proc. 23rd Power Sources Symp., Atlantic City, New Jersey, 1969*, PSC Publication Committee, Red Bank, N.J. p. 80.
304 A. Lyall *et al., Tech. Rep. AF-APL-TR-65-128*, March, 1966.
305 J. P. Gabano, V. Dechenaux, G. Gerbier and J. Jammet, *J. Electrochem. Soc., 119* (1972) 459.
306 *Li Battery Data Sheets*, P. R. Mallory and Co Inc., Burlington, Mass., 1976.
307 *Ger. Offen. 232495.*
308 *US Pat. 3716 410.*
309 *US Pat. 3726 716.*
310 *US Pat. 3716 400.*
311 *US Pat. 3887 397* (1975), to R. J. Horning.
312 *US Pat. 3413 154* (1963) to M. L. B. Rao.
313 *US Pat. 4085 256* (1978) to A. N. Dey.
314 I. A. Kedrinskii, S. V. Morozon, G. I. Suchova and T. V. Kuznezova, *Ext. Abstr. No. 152, ISC 28th Meeting*, Varna, 1977.
315 H. Taylor, *Proc. 12th I.E.C.E.C., 1977*, Vol. 1, p. 288.
316 P. M. Shah, *Proc. 25th Power Sources Symp.*, PSC Publication Comm., 1972, p. 59.
317 A. N. Dey, *Thin Solid Films, 43* (1977) 131.
318 P. Bro, R. Holmes and H. Taylor, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 703.

319 A. N. Dey, unpublished results, 1976, in A. N. Dey, *Thin Solid Films, 43* (1971) 131.

320 H. N. Seiger, A. E. Lyall and R. C. Shair, in D. H. Collins (ed.), *Power Sources 2*, Pergamon Press, Oxford, 1970.

321 K. H. M. Brauer and J. A. Harvey, *Status Rep., AD 654813*, 1967.

322 T. Ohzuku, H. Wakamatsu, Z. Takehara and S. Yoshizawa, *Electrochim. Acta, 24* (1979) 723.

323 M. S. Whittingham, *J. Electrochem. Soc., 123* (1976) 315.

324 S. Lerner and H. N. Seiger, *J. Electrochem. Soc., 117* (1970) 524.

325 P. Cignin, *Electrochim. Acta, 23* (1978) 1099.

326 F. W. Dampier, *J. Electrochem. Soc., 121* (1974) 656.

327 J. G. Gibson and J. C. Sudworth, *Specific Energies of Galvanic Reactions and Related Thermodynamic Data*, Chapman and Hall, London, 1973.

328 M. S. Whittingham, *J. Electrochem. Soc., 122* (1975) 713.

329 A. N. Dey, *Ext. Abstr. 54, Fall Meeting, The Electrochemical Society, Boston, MA, Oct. 7 - 11, 1973*, p. 132.

330 H. F. Hunger and L. J. Heymach, *J. Electrochem. Soc., 120* (1973) 1161.

331 A. J. Valerga, R. B. Badachape, G. D. Parks, P. Kamarchik, J. L. Wood and J. L. Margrave, *Final Rep., Contract DAAB07-73-C-0056*, March, 1974.

332 L. Campanella and G. Pistoia, *J. Electrochem. Soc., 118* (1971) 1905.

333 G. W. Jackson and G. E. Blomgren, *J. Electrochem. Soc., 116* (1969) 1483.

334 J. F. Hon, *Mol. Phys., 15* (1968) 57.

335 S. Lerner and H. N. Seiger, *J. Electrochem. Soc., 117* (1970) 574.

336 M. M. Nicholson, *J. Electrochem. Soc., 118* (1971) 1047.

337 P. Fiordiponti, S. Panero, G. Pistoia and C. Temperoni, *J. Electrochem. Soc., 125* (1978) 511.

338 P. Fiordiponti, G. Pistoia and C. Temperoni, *J. Electrochem. Soc., 125* (1978) 14.

339 M. S. Whittingham, *J. Electrochem. Soc., 122* (1975) 526.

340 T. Ohzuku, Z. Takehara and S. Yoshizawa, *Electrochim. Acta, 24* (1979) 219.

341 H. F. Hunger and G. J. Haymach, *ECOM-4047*, 1972.

342 Hironosuke Ikeda, Nobuhiro Furukawa and Senji Suenaga, in J. Thompson (ed.), *Power Sources 8*, Academic Press, London, 1981, p. 63.

343 M. S. Whittingham, *J. Electrochem. Soc., 123* (1976) 315.

344 P. Cignini, *Electrochim. Acta, 23* (1978) 1099.

345 M. S. Whittingham, *J. Electrochem. Soc., 123* (1976) 315.

346 W. Tiedmann, *J. Electrochem. Soc., 121* (1974) 1308.

347 T. P. Dirkse, in A. Fleischer (ed.), *Zinc–Silver Oxide Batteries*, Wiley, New York, 1971, p. 100.

348 D. W. Murphy and F. A. Trumbore, *J. Electrochem. Soc., 123* (1976) 960.

349 F. Bonino, C. Forte, M. Lazzari and B. Scrosati, *J. Power Sources, 3* (1978) 257.

350 S. Conte, V. Filippechi and G. Pistoia, *J. Power Sources, 1* (1977) 2.

351 B. Di Pietro and B. Scrosati, *J. Electrochem. Soc., 124* (1977) 161.

352 F. Bonino, M. Lazzari and B. Scrosati, *J. Electroanal. Chem. Interfacial Electrochem., 93* (1978) 117.

353 A. N. Dey and M. L. B. Rao, *Ext. Abstr. No. 53, Electrochemical Society Fall Meeting, Boston, MA, 1973.*

354 G. Lehmann, T. Rassinoux, G. Gerbier and J. P. Gabano, in D. H. Collins (ed.), *Power Sources 4*, Oriel Press, Newcastle upon Tyne, 1973, p. 493.

355 R. Messina, M. Broussely, J. Perichon and G. Gerbier, *Paper 149, 28th Meeting of the I.S.E.*, Varna, Bulgaria, 1977.

356 R, Messina, J. Perichon, M. Broussely and G. Gerbier, *J. Appl. Electrochem., 8* (1978) 405.

357 A. E. Martin, R. K. Steunenberg and Z. Tomcquk, *J. Electrochem. Soc., 121* (1974) 274C.

358 C. C. Liang, Solid state batteries, *Appl. Solid State Sci., 4* (1974) 95.

359 P. Bro, H. Y. Kang, S. Schlaikjer and H. Taylor, *I.E.C.E.C. 75 Record*, 1975, p. 432.

360 P. Bro, R. Holmes and H. Taylor, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 703.

361 S. Abens, Non-hazardous Li organic electrolyte batteries, *Power Conversion Inc. ECOM-73-04424-F, AD-A02144.*

362 D. Linden and B. McDonald, *J. Power Sources, 5* (1980) 35.

363 W. L. Leupold, Evaluation of Li/SO_2 cells under extreme temperatures storage, *Naval Air Development Center, Phase Rep. I and II,* Naval Air Development Center, Warminster, PA.

364 D. Linden, N. Wilburn and E. Brooks, in D. H. Collins (ed.), *Power Sources 4,* Oriel Press, Newcastle upon Tyne, 1973, p. 483.

365 R. G. Gunther, in D. H. Collins (ed.), *Power Sources 5,* Academic Press, London, 1975, p. 729.

366 Anon., Li/Br_2 cell systems, *Proc. Electrochem. Soc.*, 1980, No. 80/4 pp. 122 - 135.

367 Anon., *Proc. Electrochem. Soc.*, 1980, No. 80/4 pp. 187 - 194.

367 (a) *Electrochem. Abstr. No. 3116* (Jap), 1982.

368 N. G. Gutmore, P. C. Wall, B. G. Brooker and L. B. Harris, High energy batteries, *Aust. Phys., 17* (5) (1980) 8 - 83.

369 J. Broadhead, F. A. Trumbore and S. Basu, *J. Electroanal. Chem. Interfacial Electrochem. 118* (1980) 241 - 250.

370 N. S. Whittingham, *J. Electroanal. Chem. Interfacial Electrochem., 118* (1981) 229 - 239.

371 P. A. Christian, J. N. Carides, F. J. DiSalvo and J. V. Waszczak, *J. Electrochem. Soc., 127* (1980) 2315 - 2319.

372 B. M. L. Rao, Supporting electrolytes containing tetrabutylammonium ions in Li/TiS_2 cells: interaction of tetrabutylammonium ions in TiS_2, *Mater. Res. Bull., 16* (8) (1981) 919 - 922.

373 M. Voinov, On the stoichiometry of Li insertion in MnO_2, *Electrochim. Acta, 26* (10) (1981) 1373 - 1376.

374 Anon., The development of very thin Li cells, *Prog. Batteries Solid Cells,* (2) (1979) 87 - 89.

375 M. Eisenberg, The sulfospinel–Li battery system: initial study, *J. Electrochem. Soc., 127* (1980) 2382 - 2383.

376 Bi Dao-Zhi and Wang Ji-Qiang, A study of anatase–TiO_2 as cathode material for ambient temperature Li secondary cells, *Proc. Electrochem. Soc.,* No. 80/7 (1980) 245 - 260.

377 J. Wattanabe, E. Kawaklbo, M. Shinagawa and Y. Kajikawa, *Prog. Batteries Sol. Cells,* (3) (1980) 73 - 76.

378 J. O. Besenhard, Li and Li alloys in secondary organic electrolyte batteries, *Prog. Batteries Sol. Cells,* (3) (1980) 87 - 89.

379 P. Touzain and A. Jobert, *Electrochim. Acta, 26* (1981) 1133 - 1136.

380 Y. Takada, *Electrochem. Abstr., No. 2950,* 1982, Govt. Ind. Res. Inst., Osaka, Ikeda, Japan.

381 J. Epelboin, Behaviour of secondary Li and Al–Li electrodes in PC, *J. Electrochem. Soc., 127* (1980) 2100 - 2104.

382 Anon., Cycling behaviour of Li in PC–$LiClO_4$, *Prog. Batteries Sol. Cells,* (2) (1979) 96 - 100.

383 K. I. Tikhonor, B. A. Ravdel, I. A. Sokolov and L. B. Raikel'son, Electrochemical behaviour of a Li electrode in $SOCl_2$, *Elektrokhimiya, 17* (1981) 877 - 880.

383 (a) K. M. Abraham and R. M. Mark, *J. Electrochem. Soc., 127* (1980) 2091 - 2096.

384 K. I. Tikhonor, P. A. Raudel, I. A. Sokalov and L. B. Raikel'son, *Elektrokhimiya, 17* (3) (1981) 394 - 397.

385 Reliability of the Li/$SOCl_2$ in implantable pulse generators, *Proc. Electrochem. Soc.,* No. 80/4 (1980) 102 - 109.

386 Yu. M. Pavarov, Mechanism of Li passivation in $SOCl_2$, *Elektrokhimiya, 16* (1980) 1252 - 1256.

387 C. Schlaikjer and M. Dobrisin, Investigation of methods to eliminate voltage delay in

Li/SOCl$_2$ cells, *Rep. DELET/TR-78-0558-1F, GTE Lab. Inc., 1980 1-75 USNTIS, Order No. Ad-A086992.*

388 N. Marincic and J. Epestein, Recent developments in minature Li/SOCl$_2$ cells, *Prog. Batteries Sol. Cells*, (3) (1980) 84 - 86.

389 W. K. I. Stone and R. J. Brodd, *J. Electrochem. Soc., 129* (8) (1982) 1853.

390 *Prog. Batteries Sol. Cells*, (3) (1980) 74.

391 G. Bandjopadhyay, J. T. Dusek and T. M. Galvin, Development of porous sintered-ceramic separators for application in a LiAl/LiCl–KCl/FeS battery, *Ceramurgia Inst. 5* (3) (1979) 95 - 100.

391 (a) P. J. Nigrey and D. MacInness, Light weight rechargeable storage batteries using polyacetylene as the cathode-active material, *J. Electrochem. Soc., 128* (8) (1981) 1651 - 1654.

392 A. S. Baranski and W. R. Fawcett, *J. Electrochem. Soc., 129* (1982) 1.

393 S. S. Wang, Electrochemistry of dimethyl sulfite, *J. Electrochem. Soc., 128* (9) (1981) 1873 - 1877.

394 Jun-ichi Yamaki and Akihko Yamaji, *J. Electrochem. Soc., 129* (1982) 5.

395 G. E. Blomgren, Interactions in Li battery electrolyte solutions, *Proc. Electrochem. Soc.*, 80/7 (1980) 35 - 45.

396 New solvents and electrolytes of batteries, *Denki Kagaku, 48* (12) (1980) 680.

397 V. R. Koch, J. L. Goldman, C. J. Mettos and M. Mulvaney, *J. Electrochem. Soc., 129* (1) (1982) 1 - 4.

398 Lutgard C. de Jonghe, *J. Electrochem. Soc., 129* (4) (1982) 252.

398 (a) Y. Matsude, Organic electrolytes for Li batteries, *Prog. Batteries Sol. Cells*, (2) (1979) 82 - 83.

399 B. Scrosati, Non aqueous Li cells, *Electrochim. Acta, 26* (11) (1981) 1559 - 1567.

400 N. Marincic, Technology and performance characteristics of Li inorganic batteries, *Prog. Batteries Sol. Cells*, (2) (1979) 40 - 43.

401 S. B. Brummer, K. M. Abraham, V. R. Koch and G. L. Holleck, *Final Rep., Contract 4503510* to Lawrence Berkeley Laboratory by EIC Laboratories Inc., August, 1980.

402 V. R. Koch, in *Final Rep., Contract 4503510* to Lawrence Berkeley Laboratory by EIC Laboratories Inc., August, 1980, Ch. II.

403 V. R. Koch and J. H. Young, *Science, 204* (1979) 499.

404 M. S. Whittingham, *Science, 192* (1976) 1126.

405 G. H. Newman, R. W. Francis, L. H. Gavies and B. M. L. Rao, *J. Electrochem. Soc., 127* (1980) 2025.

406 K. M. Abraham, *J. Power Sources, 1* (1981) 1.

407 G. L. Holleck, K. M. Abraham and S. B. Brummer, in B. B. Owens and N. Margalit (eds.), *Proc. Symp. on Power Sources for Biomedical Implantable Applications, Ambient Temperature Lithium Batteries*, The Electrochemical Society Softbound Proceedings Series, Princeton, NJ, 1980, p. 384.

408 G. Eichinger, *J. Electroanal. Chem. Interfacial Electrochem., 83* (1977) 193.

409 M. S. Whittingham, *J. Electrochem. Soc., 123* (1976) 315.

410 M. S. Whittingham, *Prog. in Solid State Chem., 12* (1978) 41.

411 J. E. Chilton, Jr., W. J. Conner, W. J. Cook and A. W. Holsinger, *Final Rep. on Ag-33 (615)-1195, AEAPL-TR-64-147*, 1965, Lockheed Missiles and Space Co.

412 R. D. Rauh and S. B. Brummer, in D. W. Murphy and B. C. H. Steel (eds.), *Materials for Advanced Batteries*, Plenum Press, New York, 1980.

413 H. F. Baumann, J. E. Chilton, W. J. Conner and G. M. Cook, *Rep. AD 425 876*, Lockheed Space and Missiles Co., 1963.

414 R. D. Rauh and S. B. Brummer, *Electrochim. Acta, 22* (1977) 84.

415 R. D. Rauh and S. B. Brummer, *Electrochim. Acta, 22* (1977) 75.

416 J. L. Weininger and F. F. Holub, *J. Electrochem. Soc., 117* (1970) 340.

417 V. R. Koch and J. H. Young, *J. Electrochem. Soc., 125* (1978) 1371.

418 M. S. Whittingham, *Science, 192* (1976) 1176.

419 D. W. Murphy and P. E. Christian, *Science, 205* (1979) 657.

420 J. Jornie and C. W. Tobias, *J. Appl. Electrochem., 5* (1975) 279.

421 J. L. Goldman, R. M. Mank, J. H. Young and V. R. Koch, *J. Electrochem. Soc., 127* (1980) 1461.

422 R. Selim and P. Bro, *J. Electrochem. Soc., 121* (1974) 1457.

423 V. R. Koch, submitted to *J. Electrochem. Soc.*, 1978.

424 V. R. Koch and S. B. Brummer, *Electrochim. Acta, 23* (1978) 55.

425 M. B. Armand, J. B. Chabagno and M. J. Duclot, in P. Vashishta, J. N. Mundy and G. K. Shenoy (eds.), *Fast Ion Transport in Solids*, Elsevier-North Holland, Inc., New York, 1979, pp. 131 - 136.

426 L. H. Gavies, R. W. Francis, G. H. Newman and B. M. L. Rao, in *Ext. Abstr., 11th Intersoc. Energy Conversion and Engineering Conf., 1976*, pp. 418 - 423.

427 G. H. Newman, R. W. Francis, L. H. Gavies and B. M. L. Rao, *J. Electrochem. Soc., 127* (1980) 2205.

428 M. F. Lappert, *Chem. Rev., 56* (1956) 1035.

429 E. L. Muetterties, (ed.), *The Chemistry of Boron and its Compounds*, Wiley, New York, 1967, pp. 443 - 582.

430 E. Negishi, *J. Organomet. Chem., 108* (1976) 281.

431 W. E. Rhine, G. Stuchy and W. Paterson, *J. Am. Chem. Soc., 97* (1975) 6405.

432 A. Sequeire, I. Bernac, I. D. Brown and R. Faggiani, *Acta Crystallogr. B., 31* (1975) 1735.

433 F. W. Dampier and S. B. Brummer, *Electrochim. Acta, 22* (1977) 1339.

434 R. D. Rauh, T. F. Reuse and S. B. Brummer, *J. Electrochem. Soc., 125* (1978) 186.

435 B. Scrosati, *Electrochim. Acta, 26* (1981) 1559.

436 V. R. Koch and J. H. Young, *Science, 204* (1979) 209.

437 A. N. Dey, *J. Electrochem. Soc., 118* (1971) 1547.

438 M. M. Nicholson, *J. Electrochem. Soc., 121* (1974) 736.

439 B. M. L. Rao, R. W. Francis and M. A. Christopher, *J. Electrochem. Soc., 124* (1977) 1490.

440 J. R. Van Beek and P. J. Rommers, in J. Thompson (ed.), *Power Sources 7*, Academic Press, London, 1979, p. 595.

441 H. F. Baumann, J. E. Chilton, W. J. Conner and G. M. Cook, *Rep. AD 425 876*, 1963, Lockheed Missiles and Space Co., Palo Alto, CA.

442 J. O. Besenhard and G. Eichinger, *J. Electroanal. Chem. Interfacial Electrochem., 68* (1976) 1.

443 J. P. Gabano, G. Gerbier and J. F. Laurent, *Chem. Ing. Techn., 42* (1970) 210.

444 C. A. Melendres, *J. Electochem. Soc., 124* (1977) 650.

445 J. O. Besenhard, *J. Electroanal. Chem., 78* (1977) 189.

446 J. Epelboin, M. Froment, M. Carreau, J. Thevenin and D. Warin, *J. Electrochem. Soc., 127* (1980) 2100.

447 *Fr. Pat. 1,589,215.*

448 A. Caiola, J. Y. Faudou and J. C. Sohm, *21st Meeting C.I.T.C.E., Prague, 1970*, Butterworths, London, 1971.

449 B. A. Boukamp, G. C. Lesh and R. A. Huggins, *J. Electrochem. Soc., 128* (1981) 725.

450 M. S. Whittingham, *Prog. Solid State Chem., 12* (1978) 41.

451 G. L. Holleck and J. R. Driscoll, *Electrochim. Acta, 22* (1977) 647.

452 D. W. Murphy and P. E. Christian, *Science, 205* (1979) 660.

453 J. O. Besenhard, *J. Electroanal. Chem., 94* (1978) 77.

454 M. Lazzari and B. Scrosati, *J. Electrochem. Soc., 127* (1980) 773.

455 G. Eichinger and J. O. Besenhard, *J. Electroanal. Chem. Interfacial Electrochem., 72* (1976) 1.

456 R. D. Rauh, K. M. Abraham, S. B. Brummer, F. W. Dampier, G. F. Pearson and J. K. Surpenant, *U.S. Dept. of Energy, Contract No. EY-76-C-02-2520*, 1978.

457 F. W. Dampier, *J. Electrochem. Soc., 128* (1981) 2501.

458 G. Eichinger and H. P. Fritz, *J. Electroanal. Chem. Interfacial Electrochem., 58* (1975) 357.

459 J. Broadhead, in D. H. Collins (ed.), *Power Sources 4*, Oriel Press, Newcastle upon Tyne, 1973, p. 469.

460 J. Broadhead and A. D. Butherus, *U.S. Pat. No. 3791867* (1974).

461 A. D. Butherus and J. Broadhead, *Abstr. No. 10, Electrochemical Society Meeting, Miami Beach, Florida, 1972.*

462 J. Broadhead, F. A. Trumbore and S. Basu, *J. Electroanal. Chem. Interfacial Electrochem., 118* (1981) 241.

463 F. A. Trumbore, J. Broadhead and T. M. Putvinski, *Abstr. No. 61, Electrochemical Society Meeting, Boston, 1973.*

464 J. Broadhead and F. A. Trumbore, *Abstr. No. 178, Electrochemical Society Meeting, Chicago, 1973.*

465 F. A. Trumbore and J. Broadhead, *Abstr. No. 179, Electrochemical Society Meeting, Chicago, 1973.*

466 D. W. Murphy, F. A. Trumbore and J. N. Carides, *J. Electrochem. Soc., 124* (1977) 325.

467 G. L. Holleck, F. S. Shuker and S. B. Brummer, *Proc. Tenth Intersoc. Energy Conversion Eng. Conf., Newark, Delaware, 1975*, p. 444.

468 D. W. Murphy and F. A. Trumbore, *J. Electrochem. Soc., 123* (1976) 960.

469 D. W. Murphy and F. A. Trumbore, *J. Cryst. Growth, 39* (1977) 185.

470 F. A. Trumbore, *Pure Appl. Chem., 52* (1980) 119.

471 D. W. Murphy and J. N. Carides, *J. Electrochem. Soc., 126* (1979) 349.

472 D. W. Murphy, J. N. Carides, F. J. DiSalvo, C. Cros and J. V. Waszczal, *Inorg. Chem., 15* (1976) 17.

473 J. N. Carides and D. W. Murphy, *J. Electrochem. Soc., 124* (1977) 1309.

474 M. S. Whittingham, *Prog. Solid State Chem., 12* (1978) 1.

475 B. Scrosati, *Electrochim. Acta, 26* (1981) 1559.

476 M. S. Whittingham, in J. D. McIntyre, S. Srinivasan and F. G. Will (eds.), *Proc. Symp. Electrode Materials and Processes for Energy Conversion and Energy Storage*, Electrochem. Soc., Princeton, N.J., 1977, p. 784.

477 K. Yokoyama and T. Kawai, *Proc. 28th Power Sources Symp.*, The Electrochemical Society, Princeton, NJ, 1978, p. 219.

478 F. W. Dampier, *J. Electrochem. Soc., 126* (1979) 507.

479 M. Eisenberg, in *Proc. 28th Power Sources Conf.*, The Electrochemical Society, 1978, p. 155.

480 M. Einsenberg, *U.S. Pat. 4136233* (1979).

481 M. Eisenberg, *Electrochim. Acta, 26* (1981) 955.

482 D. W. Murphy, P. A. Christian, F. J. DiSalvo and J. N. Carides, *J. Electrochem. Soc., 126* (1979) 497.

483 A. J. Jacobson and S. M. Rich, *J. Electrochem. Soc., 127* (1980) 779.

484 K. Kumagai and K. Tanno, *Denki Kagaku, 48* (1980) 432.

485 G. Pistoia, C. Temperoni, P. Cignini, M. Icovi and S. Panero, *J. Electroanal. Chem. Interfacial Electrochem., 108* (1980) 169.

486 C. R. Walk and J. G. Gove, *Paper No. 27, Electrochemical Society Meeting, Toronto, May 11 - 16, 1975.*

487 P. A. Christian, J. N. Carides, F. J. DiSalvo and J. V. Woszczak, *J. Electrochem. Soc., 127* (1980) 2315.

488 D. W. Murphy, F. J. DiSalvo, J. N. Carides and J. V. Waszczak, *Mater. Res. Bull., 13* (1978) 1395.

489 W. Margelit, *J. Electrochem. Soc., 121* (1974) 1460.

490 M. Icovi, S. Panero, A. D'Agate, G. Pistoia and C. Temporini, *J. Electroanal. Chem. Interfacial Electrochem., 102* (1979) 343.

491 P. Fiordiponti, G. Pistoia, C. Temporoni, M. Icovi and S. Panero, *J. Electroanal. Chem. Interfacial Electrochem., 108* (1980) 181.

492 L. Campanella and G. Pistoia, *J. Electrochem. Soc., 129* (1982) 5.

493 J. Yamaki and A. Yamaji, *J. Electrochem. Soc., 129* (1982) 5.

494 D. MacInnes, Jr., M. A. Druy, P. J. Nigrey, D. P. Nairns, A. G. MacDiarmid and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, (7) (1981) 317.
495 J. Nigrey, A. G. MacDiarmid and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, (1979) 594.
496 R. V. Moshtev, V. Manev, A. Nassalevska, G. Pistoia and M. Icavi, *J. Electrochem. Soc., 128* (1981) 1399.
497 G. Pistoia and U. Marcinelli, *Electrochim. Acta, 22* (1977) 1141.
498 K. R. Kirk-Othmer, *Encyclopedia of Chemical Technology, 12*, Wiley, New York, 1964, p. 538.