1

STATUS OF RECHARGEABLE POSITIVE ELECTRODES FOR AMBIENT TEMPERATURE LITHIUM BATTERIES

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Summary

There have been striking advances in the technology of ambient temperature rechargeable lithium cells during the middle and late 1970s. Discoveries of new and attractive cathode systems, along with developmental efforts on some, have contributed significantly to this. A survey of the status of the positive electrodes is presented. Insoluble solid cathodes which undergo intercalation or topochemical electrode reactions appear to be the most promising for immediate application in practical cells. There are presently available several such materials suitable for fabricating cells with high energy density, rate capability, and rechargeability. It is hoped that this account will direct the attention of investigators in this area to promising systems with the result that research and developmental efforts on practical rechargeable Li batteries will be accelerated.

A. Introduction

A most important aspect in developing high energy Li cells concerns the behavior of cathode materials. During the past two decades a large variety of materials has been discovered and evaluated as reversible cathodes for Li cells. However, the degree of understanding of these materials varies considerably. Some major considerations in the development of high energy cathodes for secondary Li cells are [1]:
  high energy density;
  electrochemical reversibility;
  stability in the electrolyte;
  electrical conductivity.
Virtually all the cathode materials investigated so far have been inorganic compounds. These materials may be classified according to different criteria, but here we will distinguish between soluble/partially soluble cathodes (Section B) and insoluble, solid cathodes (Section C).

   The discussion will concentrate primarily on three aspects of the performance of each cathode material: (1) energy density; (2) rate capability; and (3) rechargeability. Other relevant aspects, such as ease of material synthesis, relative costs of materials and processes for cathode fabrication, and cathode storageability in complete cells, especially at elevated temperatures, will also be discussed, where information is available.

1. Energy density

   Lithium is the most electropositive element and is very light in weight (equivalent weight = 6.94). Hence, electrochemical cells based on Li anodes and moderately light cathodes, potentially have good energy densities. The attractiveness of a given secondary cell will, however, depend on the energy that can actually be delivered at the rate required in a particular application and the availability of this energy over a large number of cycles. Vehicle applications make the highest demands for high energy density at high rates. For example, a minimum specific energy of 200 W h/kg with a power capability of 200 W h/kg is required for an electric vehicle with performance characteristics comparable with small, gasoline-powered family vehicles [2].

   In a practical cell one can expect to obtain between 25 and 33 percent of the energy density predicted from the observed (i.e., not the theoretical) equivalent weights of the materials.

2. Rate capability

   The rate requirements for secondary Li cells depend on the particular application. For electric automobiles, an average discharge rate is perhaps 4 h, but there are many occasions where the peak power requirements are much higher. It is then most appropriate to ask what is it that limits the rate of specific non-aqueous Li secondary cells. Rate limitations may be imposed by slow electrode kinetics and poor transport phenomena either in the electrode material or in the electrolyte. With soluble cathodes, the electrode reactions often proceed at high rates, especially if the product is also soluble in the electrolyte. If the product is insoluble, any limitations caused by precipitation on the cathode current collector may be improved by increasing the electrode porosity. With insoluble cathodes, poor transport within an electrode may result from intrinsically low Li^+ diffusion in the solid material, as could be encountered in cathodes involving topochemical reactions or, more frequently, from low electrode porosity. In the former case, very little improvement is possible, but usually this is not the main rate-limiting factor and improvements are usually possible by increasing the electrode's porosity.

   The aforementioned effects notwithstanding, the rate in a nonaqueous Li cell can become limited by transport in the electrolyte and separator. A recent report by Atlung [3] gives some insight into the extent of this type of limitation. A reasonable starting point for a quantitative evaluation of the rate behavior in a Li cell is to consider a cathode having a capacity density of 15 mA h/cm^2 and 20 mil (0.5 mm) thick. For a 4 h average discharge rate,

one would have to employ a current density of 3.75 mA/cm². Assuming that the rate limitation is due to transport in the electrolyte and separator, the steady state limiting current density*, according to Atlung [3], is given by

$$i = \frac{4FC_0 D_+}{d}$$

Here, C_0 is the concentration of the electrolyte, D_+ is the diffusion coefficient of Li^+ ion, and d is the path length between the electrodes. A preferred electrolyte in secondary Li cells is 1.5M $LiAsF_6$ in 2Me-THF. A reasonable estimate for D_+ is ~ 1 - 5 × 10^{-6} cm² s^{-1}. A typical thickness for the separator is 0.05 mm. For a partially discharged cell, the cathodic reaction is displaced into the porous cathode. The tortuosity of the separator causes an increase in the real path length between the electrodes. We will assume a factor of 2. A reasonable estimate for d is then 0.6 mm (*i.e.*, 2 × 0.05 + 0.5). The value of i, then, is

$$i = \frac{4F \times 1.5 \times 10^{-3} \times D_+}{0.06} \text{ ampere.}$$

The actual current will be reduced by a factor determined by the porosity of the separator. For a separator with a volume porosity P, the free area is $1 - \sqrt{1 - P}$ [3]. For $P = 0.5$, this gives a factor, 0.3. Thus i is

$$i = 0.3 \frac{4F \times 1.5 \times 10^{-3} \times D_+}{0.06} \text{ ampere.}$$

For D_+ equal to 10^{-6} cm²/s, $i = 3$ mA/cm². For D_+ equal to 5×10^{-6} cm²/s, $i = 15$ mA/cm².

This limiting current would be reached in a period of t, the time constant for diffusive transport, given by

$$t = \frac{d^2}{4D_+} = \frac{(0.06)^2}{4 \times 10^{-6}} = \frac{3.6 \times 10^{-3}}{4 \times 10^{-6}} \sim 15 \text{ minutes.}$$

Thus, higher current densities than these should be possible for shorter periods [3]. In these situations, the limiting factor is ohmic resistance. System optimization through proper choices of solute–solvent combinations and separator materials is the answer to improving rate limitations.

3. Rechargeability

A good starting point for the present discussion of rechargeability   is that a system must still deliver the required energy and power densities (*e.g.*, 200 W h/kg and 200 W/kg) at the rated cycle life. As we show in Section 1.1.2 (p. 13), laboratory prototype Li/TiS_2 cells will deliver between 100 and 200 cycles.

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*The model of Atlung deals with the cation (Li^+) concentration profiles at the steady state situation for two plane electrodes at a distance, d, apart. A 1:1 electrolyte and single ion mobilities are assumed.

This is an interesting performance, to be considered as an unoptimized base-line for comparison with new materials.

In achieving such cycle life, it is imperative that the cathode reaction shows microscopic reversibility. But that is only the first of a number of factors to be taken into account. For example, adverse physical changes in the cathode, such as swelling during discharge, may impose limitations on rechargeability. In this case, improvements may be made through proper electrode engineering. Other factors, such as a lowered electronic conductivity of the discharged state from that of the charged state, may restrict rechargeability, especially with the high cathode loadings of practical cells. For improved electronic conductivity, additives such as carbon are often incorporated into the cathode matrix. In evaluating the performance of cathodes, as reported in the literature, it is not always possible to separate the effects of possible irreversibility of the electrode reaction *per se* from electrode structural effects. Our main emphasis is on the electrode reaction. Where appropriate, we draw attention to uncertainties in the data base because of electrode structural effects.

B. Soluble cathodes

Cells with soluble cathodes have a number of substantial potential advantages over cells with insoluble cathodes:

high rate capability;

an inherent overcharge mechanism;

little sensitivity to overdischarge;

the soluble cathode can help control dendrites at the negative electrode and maintain the Li active mass.

The major disadvantage of these cells is self-discharge. Often, the rate of self-discharge is too high (as in Li/Br_2) and/or the self-discharge product is undesirable, as for the Li/Cu halides. Attempts to limit self-discharge with ion-exchange membranes have not been successful. One difficulty is that solution conductivities are typically too low to permit the use of thick, highly nonpermeable membranes.

1. Halogens and metal halides

The highly electronegative halogens all show high voltages *vs.* Li. Table 1 shows that cells based on Li/halogen couples would exhibit very favorable theoretical energy densities. The use of F_2 as cathodic depolarizer seems to be impossible because of the very high corrosivity of this element. Gaseous Cl_2 is also difficult to handle and its solubility in organic solvents is not appreciable.
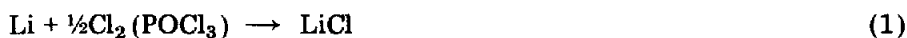
An approach involving the use of inorganic oxychlorides as solvents for Cl_2 has been suggested by Auborn *et al.* [5 - 8]. The OCV of the Li/Cl_2 cell in $POCL_3$ is approximately 4.0 V. In the presence of a Lewis acid, *e.g.*,

TABLE 1

Theoretical energy density and open cell voltages (OCV) of Li/halogen couples [4]

Reaction	OCV (V)	Specific energy (W h/kg)
$2 Li + F_2 \longrightarrow 2LiF$	6.0	6200
$2 Li + Cl_2 \longrightarrow 2LiCl$	4.0	2522
$2 Li + Br_2 \longrightarrow 2LiBr$	3.4	1047
$2 Li + I_2 \longrightarrow 2LiI$	2.8	590

$AlCl_3$, the OCV increases to 4.3 V, since the formation of $LiAlCl_4$ from LiCl and $AlCl_3$ has a negative free energy. The Li reaction with Cl_2 is apparently reversible, eqns. (1) and (2).

$$Li + \tfrac{1}{2}Cl_2(POCl_3) \longrightarrow LiCl \tag{1}$$

$$Li + \tfrac{1}{2}Cl_2(POCl_3) + AlCl_3 \longrightarrow LiAlCl_4. \tag{2}$$

Other oxychlorides such as $SOCl_2$ and SO_2Cl_2 are also possible solvents. The major present interest in oxyhalide solvents is, however, centered on their own irreversible "catalytic" reduction at solid electrodes, e.g., carbon. The oxychlorides show high voltages vs. Li and primary $Li/SOCl_2$ [9, 10], and Li/SO_2Cl_2 cells [11] are actively being developed as high energy density power sources. Because of the ready reduction of the oxychlorides themselves, they are not suitable as solvents for secondary Li–halogen cells.

Bromine can be dissolved in organic solvents, e.g., propylene carbonate (PC). Contact between Br_2 and Li must be avoided to prevent direct chemical reaction, i.e., self-discharge. The discharge product, LiBr, is soluble in most organic solvents and the Li electrode is not protected. In the investigation by Weininger et al. [12], the self-discharge was mostly eliminated by the use of an ultrafine porous polyethylene separator (ion exchange membranes were not favorable because of their high resistivity). The cell consisted of LiBr, $LiClO_4/PC$ at the anodic side, and Br_2, LiBr/PC at the cathodic side. The cathodic cell reactions supposedly are:

$$3/2Br_2 + e^- \rightarrow Br_3^- \tag{3}$$

$$Br_3^- + 2e^- \rightarrow 3Br^-. \tag{4}$$

The cell allegedly exhibited good cycling behavior. Table 2 summarizes the cycling results given as the percentage of charge recovered on discharge as a function of cycle life.

Rates of up to 1.1 mA/cm^2 have been achieved. Self-discharge was not completely eliminated in this cell by porous membranes. Self-discharge became evident after standing on open circuit for periods up to several days. It was reported that the cell does subsequently accept a fresh charge with good performance. A self-discharge rate within reasonable limits is possible

6

TABLE 2

Utilization (current efficiency) of lithium–bromine cell on continuous cycling

Cycle number	0 - 100	100 - 300	300 - 1785
Approximate utilization (%)	90	70	30

only with better separators, porous or ion-exchange type. No breakthrough has been reported yet.

In principle, a Li/I_2 cell working in an analogous manner could be made. There appears to be one reported demonstration of such a cell [13, 14].

In the early days of Li battery development, considerable effort was made to use various metal halides as cathode materials. The materials chiefly investigated were AgCl by Chilton et al. [15], AgF, AgF_2 by Shaw et al. [16], $CuCl_2$ by Herbert et al. [13], CuCl by Gabano et al. [17, 18], and CuF_2 by Boden et al. [19, 20]. Other materials such as NiF_2 and $NiCl_2$ by Sieger et al. [21], were also examined as possible candidates.

The overall reaction in these systems during cycling is

$$nLi + MX_n \rightarrow nLiX + M. \tag{5}$$

The cell voltages and theoretical energy densities of many Li/metal halide couples are shown in Table 3. The materials all provide cells with relatively high voltages and theoretical energy densities. Reversibility of the cathode reaction in each case is also good.

TABLE 3

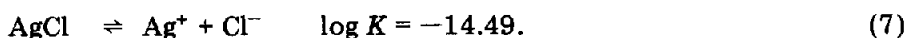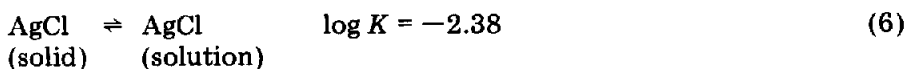Theoretical energy density and open cell voltages (OCV) of some Li/metal halide couples

Reaction	OCV (V)	Specific energy (W h/kg)
Li + AgCl $\rightarrow$ LiCl + Ag	2.85	507
Li + AgF $\rightarrow$ LiF + Ag	3.30	660
Li + CuCl $\rightarrow$ LiCl + Cu	2.80	697
2Li + $CuCl_2$ $\rightarrow$ 2LiCl + Cu	3.10	1096
2Li + CuF_2 $\rightarrow$ 2LiF + Cu	3.60	1645

For example, the $Li/CuCl_2$ system can be discharged at quite high rates, and the data of Eisenberg [22] indicate a 2.3 V plateau at the 2 h rate with a capacity of ~ 60 - 70 W h/lb. At the 5 h rate, more than 140 W h/lb are obtained. More than 50 cycles have been achieved.

According to Gabano *et al.* [17, 18], the Li/CuCl system can be discharged at the C/4 rate without damage to the reversible CuCl electrode. The charge rate could not exceed C/20, however, and the limit on the number of cycles was apparently due to the positive electrode.

Although metal fluorides are preferred as cathode materials because of their low equivalent weights, the discharge product, LiF, is insoluble in most organic solvents and this poses rate problems. High rate discharges have been demonstrated with metal chloride cathodes, as indicated above.
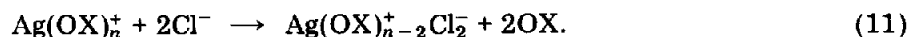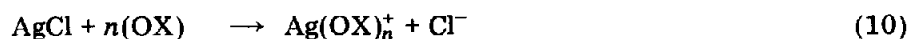
The major problem with the metal halide cathode cells results from self-discharge due to excessive solubilities of the cathode materials in the electrolyte. The problem may be explained in respect of the Li/AgCl system [4]. The solubility of AgCl in DMF is about 1×10^{-4} mol/liter. To this solubility the following equilibria may contribute:

$$AgCl \rightleftharpoons AgCl \qquad \log K = -2.38 \qquad (6)$$
$$(solid) \quad (solution)$$

$$AgCl \rightleftharpoons Ag^+ + Cl^- \qquad \log K = -14.49. \qquad (7)$$

From the above equilibria, the self-solubility of silver halides would appear to be sufficiently low. However, the ability of Ag halides to form soluble complexes with the excess halide produced in discharge reactions (eqns. (8) and (9)) may result in a serious self-discharge problem.

$$AgCl + Cl^- \longrightarrow AgCl_2^- \qquad (8)$$

$$AgCl_2^- + Cl^- \longrightarrow AgCl_3^{2-}. \qquad (9)$$

In organic solvents, reactions (7) and (8) may be written as shown in eqns. (10) and (11).

$$AgCl + n(OX) \longrightarrow Ag(OX)_n^+ + Cl^- \qquad (10)$$

$$Ag(OX)_n^+ + 2Cl^- \longrightarrow Ag(OX)_{n-2}^+Cl_2^- + 2OX. \qquad (11)$$

Here, OX is an organic solvent having donating atoms such as O, N, and S. Because Cl^- shows a stronger Lewis basicity than organic solvents, complex formation is preferred. Silver fluorides, bromides, and iodides also form soluble complexes. The fluorides NiF_2 [23], CuF_2 [19], HgF_2 [24], and CdF_2 [25], which do not form complexes exhibit much poorer discharge behavior. The reversibility of the cathode reaction in these cases is also poor. An approach to solubilize the discharge product LiF and, hence, to improve the rate characteristics has been to use a Lewis acid such as BF_3 or PF_5 so that the reversible cathode reaction is:

$$NiF_2 + 2Li^+ + 2BF_3 + 2e^- \rightleftharpoons Ni + 2LiBF_4. \qquad (12)$$
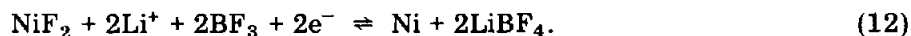
Evidently, self-discharge is excessive in this case.

It is clear that except for the high self-discharge rate due to excessive cathode solubility, Li secondary cells with metal halide cathodes should be quite attractive. An approach to avoid problems arising from formation of soluble complex species has involved the use of ion exchange membranes as

separators between the anode and cathode compartment of a cell [26 - 29]. However, the actual resistance of the ion exchange membranes is in the order of magnitude of 10^3 - 10^5 Ω (specific resistance: 10^5 - 10^7 Ω cm). These values are substantially higher than the electrolyte resistance (in contrast to the results obtained in aqueous solutions). This high resistance might be reduced by: (1) increasing the ion exchange capacity and/or (2) decreasing the thickness of the membranes. Both of these approaches should be feasible, but this approach seems to have been abandoned.

A research group led by Armand [30] in France has apparently developed some new membrane materials exhibiting superior performance. However, to our knowledge, nothing has been published yet on their performance in Li cells.

2. Soluble S cathode

Because of its high abundance at low cost, S would be an extremely attractive positive electrode. The cell voltage is $\sim$ 2.2 and the system has excellent specific energy (2570 W h/kg for the reaction $2Li + S \rightarrow Li_2S$). The feasibility of a secondary Li/S cell utilizing organic electrolytes has been extensively investigated, particularly at EIC [31, 32]. Studies of the redox chemistry of S in organic solvents have shown that S reduction proceeds *via* a series of, in general, soluble polysulfide species prior to the formation of the ultimate reduction product, insoluble Li_2S [33]. Both S and Li_2S are electronic insulators and they are insoluble in most relevant organic solvents. Thus, in the absence of an electronic conductor on the cathode, the Li/S cell would behave poorly. The rather low solubilities of S and Li_2S could also limit rate capabilities of the system [34 - 36]. A considerable research effort has thus been focussed on solubilizing the S [32].

The best success to date has been achieved with an approach in which the S has been initially incorporated in the cell as dissolved Li_2S_n [31, 32]. Hence, the theoretical cell reaction is:

$$\left(2\frac{n}{m} - 1\right) Li + S_n^{2-} \longrightarrow \frac{n}{m} S_m^{2-} + \left(2\frac{n}{m} - 1\right) Li^+. \tag{13}$$
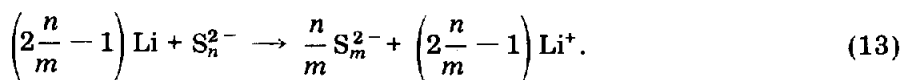
Organic solvents such as tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) have been found to dissolve greater than 10M S as Li_2S_{10}. These solvents also dissolve appreciable amounts of lower order polysulfides, Li_2S_n, $n \geqslant 2$. However, the solubility of Li_2S in these solvents is extremely low. Reasonable good cathode utilization at moderate rates has been achieved with the use of a porous catalytic cathode comprising Teflon-bonded carbon of the type used in $Li/SOCl_2$ cells [10]. The insoluble Li_2S discharge product is stored in the porous carbon electrode and, presumably, rate-capacity behavior is determined by the carbon electrode.

What has been achieved to date are: cathode utilizations of 1.5 e^-/S for 5M S as Li_2S_{12} in THF/LiAsF$_6$ at 0.5 mA/cm^2 ($\sim$ C/30 rate) at room temperature; 1.83 e^-/S for the same solution at the same rate at 50 $^\circ$C,

$1e^-/S$ for the same solution at 4 mA/cm^2 at room temperature. A cathode utilization of 1.5 e^-/S for 5M S as Li_2S_{12} and a cell voltage of 2.0 could produce practical cells with specific energies of > 110 W h/kg [31].

To date, only moderate rechargeability has been achieved. Greater than 100 low capacity (0.1 e^-/S) cycles have been demonstrated, with average efficiency approaching 100% at room temperature and 95% at 50 °C. At a depth of 0.5 e^-/S, efficiencies are about 95% at 25 °C and 90% at 50 °C, although these efficiencies tend to deteriorate after 10 - 20 cycles. The Li cycling efficiency in these cells has been determined to be, within experimental error, the same as that of the total cell. Therefore, no Li dendrites are isolated on the Li electrode during cycling. All of the Li electrodeposited during charge is either stripped during discharge or redissolved *via* self-discharge. This maintains the material balance in the cell, a major requirement for its practical success. It appears that cathode rechargeability is limited by a self-discharge mechanism whereby the S accumulates on the negative as Li_2S. The rechargeability, and probably the rate capability, would be improved by dissolution of Li_2S. A possible approach would involve the use of complexing agents such as BF_3 which form soluble complexes with Li_2S. However, this may reduce the shelf life of the cell as the protection afforded to the Li electrode by insoluble Li_2S would be eliminated.

C. Insoluble solid cathodes

It is clear from the discussions in the previous section that soluble cathodes have not, to date, achieved their promise, and that the most fruitful approach to practical Li secondary cells in the near future would be to use insoluble cathodes. Cathodes in which the Li reaction involves a displacement process, resulting in extensive bond breakage and atomic reorganization, are generally not reversible near room temperature. The most extensively studied and promising materials are those which undergo intercalation or topochemical reactions with Li and we shall confine our discussion to this class of materials.

An ideal intercalation reaction involves the interstitial introduction of a guest species into a host lattice without structural modification of the host. Such a reaction is reversible because similar transition states are readily achieved for both the forward and reverse reactions, leading to close compliance with the thermodynamic principle of microscopic reversibility [39]. In an actual intercalation reaction, the bonding within the host lattice may be slightly perturbed (*e.g.*, a slight expansion of the host lattice may occur). The inherent reversibility of intercalation suggests its utility as a mechanism for reversible electrode reactions (eqn. (14)).

$$x Li^+ + x e^- + MY_n \rightleftharpoons Li_x MY_n. \tag{14}$$

Similar reactions which depend on the structure of the host but result in somewhat larger structural modifications, such as cleavage of certain bonds,

are termed topotactic or topochemical. These reactions may be either reversible or irreversible depending upon the specific nature of the structural changes.

A number of authors, (Steele [38], Heyne [39], Whittingham [40], and Worell *et al.* [41], have proposed the following basic requirements for such solid state cathode materials:

(i) large free energy of reaction ΔG (affording a high cell voltage);

(ii) wide compositional range, *i.e.*, x in eqn. (14) (resulting in high cell capacities);

(iii) high diffusivity of the guest species (Li) in the host (allowing high power densities);

(iv) minimal structural change as a function of composition, resulting in a reversible reaction and long cycle life;

(v) good electronic conductivity.

Much of the recent research and development activities on reversible cathodes for secondary Li cells has involved these types of solid state materials. Materials which have been found to undergo topochemical or intercalation Li reaction are: transition metal sulfides, selenides or oxides with layered structures, and transition metal sulfides or oxides with three-dimensional network structures. Several reviews dealing with the structural chemistry of these compounds and its relationship to electrochemical reactions have already appeared [37, 40, 42 - 44]. We review the data on these classes of materials in the sections that follow.

1. Layered sulfides, selenides, and oxides of transition metals

The most extensively studied materials are the layered transition metal disulfides and diselenides. They generally undergo a 1 e$^-$ reaction with Li. Several trisulfides and triselenides with layered structures are known and have been investigated as rechargeable cathodes. The layered NbSe$_4$ [78] was evaluated briefly. Among the oxides, the layered oxychlorides, FeOCl, VOCl, and CrOCl have structures somewhat similar to the dichalcogenides. Their possible suitability as cathodes for secondary Li cells has received brief attention. Another layered oxyhalide studied is UO$_2$F$_2$.

1.1. Transition metal dichalcogenides, MX_2; $X = S$ or Se

The transition metal dichalcogenides, MX_2, where $X = S$ or Se and $M =$ Ti, Zr, Hf, V, Nb, Ta, Mo, and W have been investigated as cathode materials to varying degrees [40]. Pure CrS$_2$ has not been reported, but LiCrS$_2$ has been studied briefly. In addition, a series of mixed metal disulfides represented by $MXN_{1-x}S_2$, where $N = Cr$ or V and $M = Fe$, Ni, Co or Cr has been evaluated [45 - 47]. From an energy density standpoint the most preferred materials are the disulfides of the first row transition metals. These compounds are also the most extensively studied. The diselenides of the first row transition metals and disulfides and diselenides of the 2nd and 3rd row transition metals, when they meet the criteria of reversibility, rate capability, and other relevant battery requirements, may find special applications. We discuss the latter group of compounds first.

1.1.1. The dichalcogenides of the second and third row transition elements

ZrS$_2$. Reaction with n-BuLi* resulted in an uptake of one Li per mole of ZrS$_2$ to form LiZrS$_2$ (Whittingham and Gamble [49]). In the lithiated product, however, a tripling of the C lattice occurs to form a 3-block structure rather than the one-block structure observed for ZrS$_2$ itself. Cyclic voltammetry data showed the presence of both reduction and oxidation peaks, indicating intrinsic reversibility of the sulfide. Reversibility characteristics in actual Li cells have not been demonstrated, however. The structural data, which show more than modest crystallographic changes during Li intercalation, suggest that cathode rechargeability would be poor. The theoretical specific energy of this cathode with 1 e$^-$/ZrS$_2$ utilization at 2.0 V would be 330 W h/kg.

ZrSe$_2$. Reaction with n-BuLi suggests a capacity of 1 e$^-$/ZrSe$_2$ [49]. Structural data indicate a simple expansion of the C lattice by $\sim$ 0.5 Å with no rearrangement of the anion lattice. One would expect fairly good reversibility for this cathode. However, no electrochemical data are available. An estimated theoretical specific energy is 190 W h/kg.

HfS$_2$. No electrochemical data are available. Structural studies of Whittingham and Gamble [49] on the lithiated product obtained from the n-BuLi reaction indicate behavior similar to that of ZrS$_2$. An estimated theoretical specific energy would be 215 W h/kg.

HfSe$_2$. No electrochemical study has been reported. Structural studies by Whittingham and Gamble [49] on the n-BuLi reaction product indicate behavior similar to that of ZrSe$_2$. The estimated theoretical specific energy is 140 W h/kg.

NbS$_2$. Whittingham and Gamble [49] found that Nb$_{1.09}$S$_2$ reacted with n-BuLi to form Li$_{0.78}$Nb$_{1.09}$S$_2$ after 15 days' reaction. Apparently the indiffusion of Li here is very slow. Both the parent and the lithiated disulfide have the 3R rhombohedral structure. Electrochemical studies of this material have been carried out by Holleck *et al.* [50 - 52]. They obtained a cathode utilization of 0.9 e$^-$/NbS$_2$ in the first discharge. However, this capacity decreasd to $\sim$ 0.6 e$^-$/NbS$_2$ in the second cycle and remained steady at this value during subsequent cycles. Only low rate cycling has been carried out. At 0.33 mA/cm^2, the capacity in the 30th cycle was $\sim$ 0.6 e$^-$/NbS$_2$. Based

*The n-BuLi reaction mimics cell discharge [37, 48] and provides a convenient way of screening potential cathode materials. In general, a material which does not react with n-BuLi would not be expected to show electrochemical activity, although the converse is not true.

on this cathode utilization and an average cell potential of 2.0 V, the specific energy of the cathode would be 199 W h/kg.

NbSe$_2$. Reaction with n-BuLi leads to the formation of LiNbSe$_2$, indicating a maximum capacity of one Li/mole of NbSe$_2$ [49]. Electrochemical studies of Whittingham *et al.* [40] indicated that the discharge capabilities were strongly dependent on the method of preparation of the selenide. Some commercial samples apparently showed less than 5% utilization even at current densities of 50 μA/cm^2. The best cycling results of Whittingham *et al.* showed a capacity of 80% utilization in the first discharge at 0.5 mA/cm^2 and 55% utilization at 2 mA/cm^2. However, this capacity fell off rapidly, diminishing, for example, to 25% on the third discharge. This low reversibility, coupled with its high equivalent weight, make this material of little practical interest.

TaS$_2$. Two polytypes of this disulfide, namely the 1T and 2H modifications, have been investigated. Both forms take up a maximum of 1 Li/TaS$_2$ by reaction with n-BuLi. Lithium intercalation of the 2H form occurs with simple expansion of the lattice, while in the 1T modification the structure switches over to a multiblock modification upon Li intercalation. N.m.r. studies of Li$_x$TaS$_2$ revealed a lower Li diffusivity, *i.e.*, $\sim$ 2 orders of magnitude less than in TiS$_2$ [53]. The actual cathode utilization found in Li cells is only about 0.6 Li/TaS$_2$ at 1 mA/cm^2 in the first discharge [40, 54]. Apparently, the cathode has good reversibility with an average of $\sim$ 40% utilization. The lower utilization may be related to low diffusion coefficients at the extremes of lithium content. The specific energy, based on an average utilization of 60% (the first discharge) and an average cell potential of 2.0 V, is only 130 W h/kg.

MoS$_2$. This material is of interest because of its relatively low cost. Crystalline MoS$_2$ (Besenhard *et al.* [55]; Whittingham [40]) and amorphous* MoS$_2$ (Jacobson *et al.* [56]) have been evaluated as cathodes for secondary Li cells. Reaction of n-BuLi with crystalline MoS$_2$ led to the formation of Li$_2$S [49]. Electrochemically, only 0.1 Li/MoS$_2$ were utilized, suggesting that the crystalline material has little practical interest.

Considerably improved electrochemical performance was shown by a material described as amorphous MoS$_2$ [56]. This material is prepared from the normal temperature reaction of Li$_2$S with molybdenum chloride. Apparently, MoS$_2$ with varying degrees of amorphous character can be prepared by appropriate heat treatment of the material prepared at normal temperature. Using a material which had been heat-treated at 150 °C, Jacobson *et al.*

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*Amorphous materials are those which lack the long range order found in crystalline compounds. Consequently, amorphous materials do not exhibit sharp Bragg peaks in their X-ray spectra as shown by crystalline compounds.

obtained a capacity of 0.83 e^-/MoS_2 in the first discharge. This is a remarkable improvement over the crystalline material. In the second discharge the capacity decreased to ~ 0.7 e^-/MoS_2. However, according to the authors, the material has good rechargeability. Thus, even after 244 discharge/charge cycles, the capacity exceeded 50% of that of the 2nd discharge. To date only low-rate, $i.e.$, 0.5 mA/cm^2, cycling has been demonstrated. Reasons for the superior performance of the amorphous material are not clearly understood. Nevertheless, the electrochemical behavior of amorphous MoS_2 suggests that amorphous materials in general (see later) should merit considerable future research and development interest. The specific energy of MoS_2 with 0.8 e^-/mole utilization at 2.0 V is 255 W h/kg.

$MoSe_2$. No data on the electrochemical behavior of $MoSe_2$ in Li cells have been reported. Reaction with n-BuLi consumed 0.5 Li/mole of $MoSe_2$ [48]. However, this reaction apparently leads to the destruction of the $MoSe_2$ lattice, forming Li_2Se.

WS_2 and WSe_2. No electrochemical data on the behavior of these compounds in Li cells are reported. Reaction of WS_2 with n-BuLi consumed 0.3 Li/mole of WS_2, and reaction of WSe_2 with n-BuLi consumed 1.5 Li/mole of WSe_2. In both cases, however, the chalcogenide lattice was destroyed [48].

1.1.2. Dichalcogenides of the first row transition metals

TiS_2. TiS_2 is the most extensively studied of all the dichalcogenides. It is also the material on which the most extensive development work as a cathode material for secondary Li cells has been carried out. This interest has been due to the fact that the physical and chemical properties of TiS_2 more or less ideally satisfy the various criteria required by secondary cathodes. Whittingham has discussed this recently [40], quote:

"The reaction Li + TiS_2 takes place with a high free energy of reaction, 206 kJ/mole, and with little change in free energy over the composition range. There is a single phase over the entire composition range, so that no energy is expended in nucleating a new phase; in addition the lattice expands by only 10%, which should not cause substantial mechanical degradation problems, and as will be shown shortly, the entire range of x in $Li_x TiS_2$, $0 < x \leqslant 1$ values is accessible to electrochemical cycling. The diffusivity of the lithium ions is high, sufficient to permit high current densities and hence good power densities. TiS_2 is a good electronic conductor, showing semimetallic behavior, and so in principle there is no need to add conductive diluents, such as carbon, to the cathode structure. No solubility of TiS_2 was found in the organic solvents commonly used in lithium batteries. The reversibility of the reaction with Li was shown by constructing cells and cycling them."

Electrochemical studies with TiS_2 were done in cells of the configuration,

Li/Organic Solvent, Li^+ ion/TiS_2.

Most of the work* on this system was done by research groups at EIC Corporation [50 - 52, 57] and Exxon Corporation [40, 58 - 61]. Researchers at Exxon used as organic solvents dioxolane or dimethoxyethane (DME) with $LiClO_4$ or $LiB(C_6H_5)_4$ as the solute. In most of the early work at EIC the
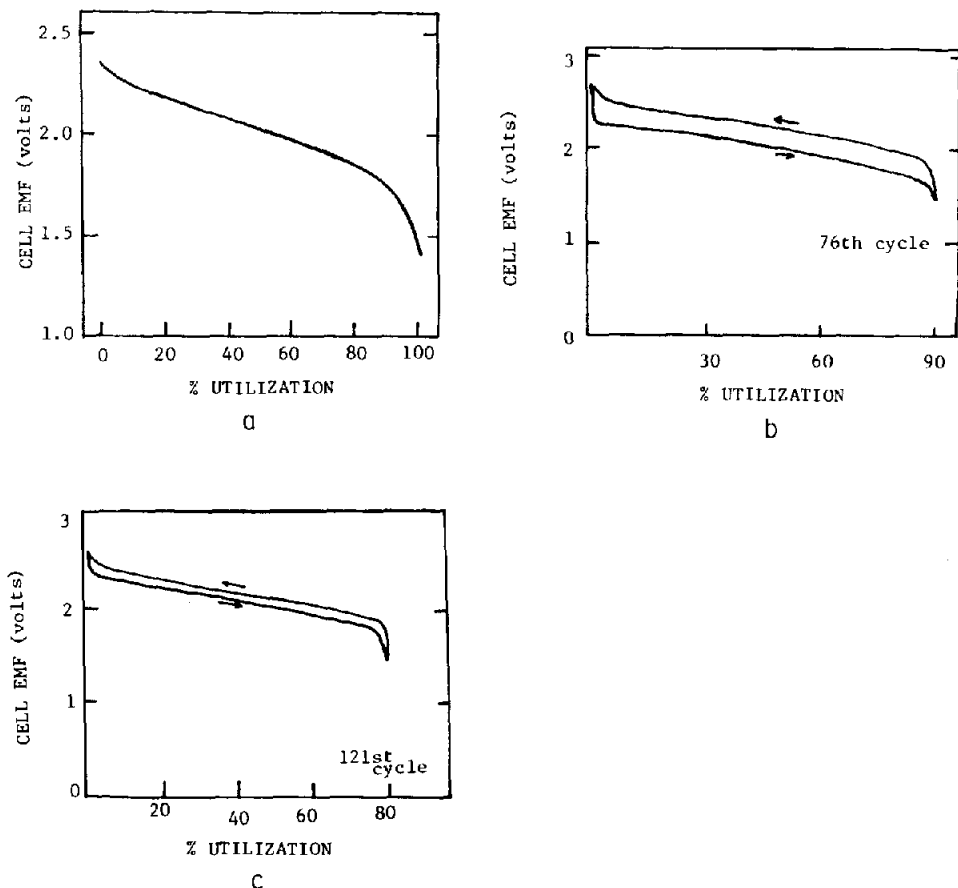

Fig. 1. Discharge and cycling curves for Li/TiS_2 cell. (a) First discharge at 10 mA/cm^2, (b) 76th cycle at 10 mA/cm^2, (c) 121st cycle at 2 mA/cm^2. (Whittingham, ref. 40.)

*Broadhead et al. in 1972 conceived the idea of holding electrochemically active materials such as iodine and S in a host matrix of a dichalcogenide such as TiS_2 and in particular, $NbSe_2$. He believed the dichalcogenides to be inactive by themselves. (J. Broadhead, in D. H. Collins (ed.), *Power Sources 4*, Oriel Press, Newcastle Upon Tyne, England, 1973; *U.S. Patent 3,791,867*; F. A. Trumbore, J. Broadhead and T. M. Putvinski, *Abstract 61*, Fall Meeting of the Electrochemical Society, Boston, MA, 1973).

organic solvent was either propylene carbonate (PC) or methylacetate (MA) with LiClO$_4$ as the solute. The recent development work at EIC (Holleck *et al.*, 1979) on practical Li/TiS$_2$ cells was carried out using 2Me-THF/LiAsF$_6$ electrolyte [62, 63].

The excellent reversibility of the cathode reaction is shown by the data for two cells in Fig. 1, one discharging at 2 mA/cm^2 on its 121st cycle and the other at 10 mA/cm^2 on its 76th cycle (Whittingham [40]). The high rate capacity of the cathode is indicated by the fact that almost complete cathode utilization (1e$^-$/TiS$_2$) was found even at 10 mA/cm^2. These studies of Whittingham and coworkers apparently were carried out with very low cathode loadings.

In the recent studies at EIC, (Holleck *et al.* [57]), tests were carried out with Li/TiS$_2$ cells having cathode capacities of ~ 15 mA h/cm^2. The electrolyte was 2Me-THF/1.5M LiAsF$_6$. Discharge and charge were carried out at constant current between preset voltage limits of 1.6 V and 3.0 V at the 6 - 10 h rate (1.5 - 2.5 mA/cm^2). Although this represented an unusually severe test regime not commonly used in evaluating cycle life of conventional rechargeable cells, the Li/TiS$_2$ cells exhibited very good performance characteristics. Cathode capacities ranged from 0.8 e$^-$/TiS$_2$ to 1.0 e$^-$/TiS$_2$ in the first discharge. The voltage–time behavior showed practically no change upon cycling (Fig. 2). Cell capacity as a function of cycle number for a typical cell is shown in Fig. 3. The capacity, which was limited by the cathode, declined slowly. However, it was found that by reducing the discharge current the capacity loss could be recovered. This work showed that the major cause for declining cathode performance in "practical Li/TiS$_2$ cells" would be changes in electrode structure with cycling. Thus, although both TiS$_2$ and LiTiS$_2$ are electronic conductors, cathodes incorporating carbon exhibited performance superior to those containing no carbon. The TiS$_2$
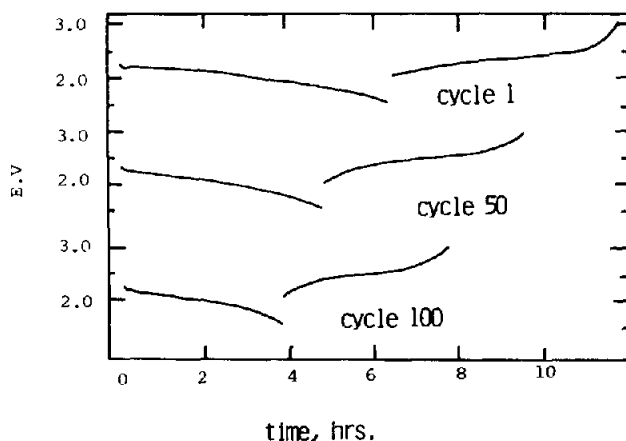

Fig. 2. Cycling curves of an Li/TiS$_2$ cell utilizing 2Me-THF/1.5M LiAsF$_6$ at cycles 1, 50 and 100. Theoretical capacity ~ 15 mA h/cm^2. (EIC Data.)
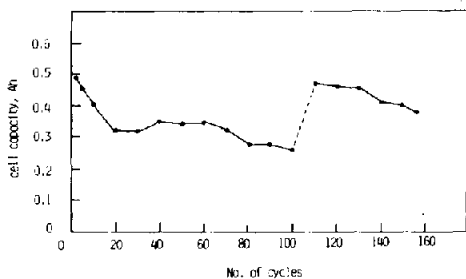
Fig. 3. Cathode utilization of an Li/TiS_2 cell during extended cycle testing. Current reduced to half of the original value from cycle 110. Cathode capacity, $\sim$ 15 mA/cm^2. (EIC Data.)

crystallites show a largely reversible expansion and contraction upon inter-calation and expulsion of Li. Thus an initially optimized electrode structure changes even after the first discharge–charge cycle, since bonded powder electrodes used in most of these studies do not show ideal elastic behavior. In the absence of C in the electrode matrix, a loss of particle-to-particle con-tact occurs, leading to diminished performance. This effect is responsible for the high cathode utilization during the early discharges and the capacity decline on later cycling of the cell, shown in Fig. 3. Reducing the current minimizes these effects. Evidently, a major area of research for developing practical TiS_2 cathodes would involve electrode engineering. Initial studies on the shelf-life of EIC $LiTiS_2$ cells show very little capacity losses after storage for 2 weeks at 90 °C. The cells did exhibit some voltage delays, however [64].

In practical configuration, although Li^+ ion transport in the separator and in the electrolyte is the ultimate rate-limiting factor, several factors relating to both chemical and physical properties of TiS_2 are also important for good rate performance. For example, the best performance is exhibited by materials having the composition, $Ti_{1.0}S_2$. Compositions between $Ti_{1.0}$-S_2 and $Ti_{1.1}S_2$ can be obtained, and may be present together, depending upon the synthetic technique [65, 66]. The higher Ti content samples exhib-it inferior rate and reversibility characteristics. A reason for this is that the excess titanium causes a pinning of the sulfide layers, which will reduce the diffusion rate of the Li^+ ions, and at the same time occupies some of the sites where the Li^+ would otherwise reside. Thus, the composition $Ti_{1.1}S_2$ shows much poorer rate behavior than $Ti_{1.0}S_2$, even though they are of comparable particle sizes. In general, the effect of stoichiometry on rate per-formance is significant in most Li intercalating cathodes.

A major concern with TiS_2 cathodes is cost. Titanium is expensive and the processing cost for "battery grade" TiS_2 is relatively high. The relatively less expensive synthesis procedures presently available for "non-battery grade" TiS_2 [67] may be upgraded to meet battery specifications. Apparent-ly, some progress has been made at Exxon in this regard.

The specific energy of TiS_2 based on 1 e^-/TiS_2 and 2.1 V is 480 W h/kg. Projected energy densities for practical Li/TiS_2 cells based on the recent EIC data are given in Fig. 4(a) and (b).
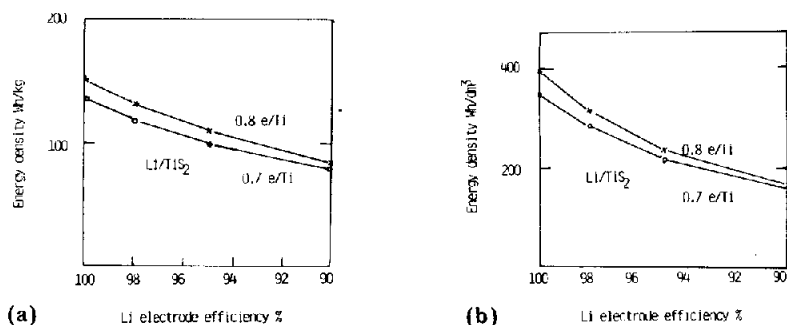

(a)   (b)

Fig. 4. (a) Projected gravimetric energy densities for practical rechargeable Li cells (100 cycles, $\sim$ D-size). (EIC Data, ref. 57.) (b) Projected volumetric energy densities for practical rechargeable Li cells (100 cycles, $\sim$ D-size). (EIC Data, ref. 57.)

Recently, Murphy [68] has shown that TiS_2 intercalates a second Li at $\sim$ 0.50 V $vs.$ Li^+/Li. This Li is rechargeable, although rechargeability decreased with cycling. The low potential of the second discharge is not practically attractive. However, Murphy has suggested that the low potential of the $LiTiS_2/Li_2TiS_2$ $vs.$ Li^+/Li might make it an attractive anode in cells of the type $Li_2TiS_2/Li^+/TiS_2$, yielding $\sim$ 1.5 - 1.9 V, and possibly circumventing the Li anode plating inefficiency.

A similar concept was used by Lazzari et $al.$ [69] in the construction and cycling of a Li cell, $LiWO_2/LiClO_4$, PC/TiS_2. The cell had an OCV of 2.0 V at 25 °C. In low rate cycling (0.10 mA/cm^2), more than 68 cycles have been achieved. The data were presented as preliminary with no details of cathode utilization. Although this concept is an interesting one, the major disadvantages would be lower cell voltages and lower energy densities than are possible with Li metal anodes.

$TiSe_2$. A limited amount of work has been done on $TiSe_2$ [40]. Reaction with n-BuLi led to the uptake of 0.97 $Li/TiSe_2$ [49]. Electrochemical studies in Li cells showed cathode utilizations of 0.95 $e^-/TiSe_2$ at 0.5 mA/cm^2, 0.75 $e^-/TiSe_2$ at 1 mA/cm^2, and 0.5 $e^-/TiSe_2$ at 2 mA/cm^2 in the first discharge. The cathode apparently exhibits good reversibility. A potentially high rate capability of this cathode is suggested by the high self-diffusion of Li^+, similar to that found in TiS_2 [53]. Nevertheless, because of the relatively lower energy density of $TiSe_2$, it does not offer any advantage over TiS_2. At 95% cathode utilization, with an average cell voltage of 1.9 V, the specific energy of the cathode is 227 W h/kg which is only half that of TiS_2.

VS_2. Unlike TiS_2, VS_2 does not show acceptable electrochemical performance at room temperature (Murphy *et al.* [45, 70]). Up to 1 Li/VS_2 can be incorporated by reaction with n-BuLi. However, in a Li cell a maximum of only 0.4 Li/VS_2 could be incorporated even at very low current densities. The Li reaction is reversible but the capacity decreases with cycling, even at the very low level of cathode loading and the low rates employed in Murphy's experiments. The poor performance of VS_2 results from the presence of two slightly distorted phases in $Li_x VS_2$ near $x = 0.33$ (α-phase) and $x = 0.5$ (β-phase). Murphy's preliminary results seemed to indicate that above 85 °C, $Li_x VS_2$ is a single phase for $0 < x < 1$, with the result that better cycling occurs above this temperature. Because of the higher voltage of Li/VS_2 cells (*i.e.*, 0.2 V more than in Li/TiS_2 cells), this material may find special applications in high temperature batteries.

VSe_2. The suitability of this cathode material was investigated by Whittingham, at Exxon [40, 71]. Reaction with n-BuLi resulted in an uptake of more than 1.5 Li/VSe_2, suggesting the possibility of high Li capacity for this cathode. Cycling studies in Li cells showed exceptionally high cathode utilizations at rates between 1 and 10 mA/cm^2 (Fig. 5). The reversibility of this cathode is also very good, being very similar to that of TiS_2. The 22nd cycle for a cell discharging at 2 mA/cm^2 is shown in Fig. 6. It was also found that at potentials between 1.4 V and 1.0 V a second Li could be incorporated with apparent ready reversibility [68, 71].
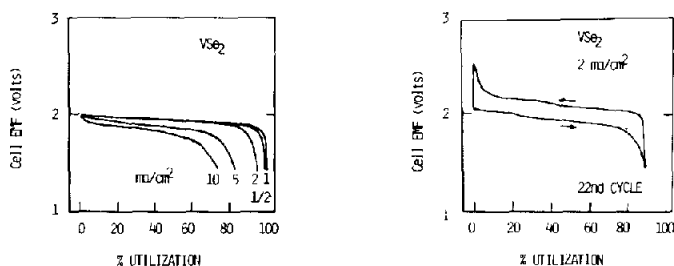

Fig. 5. First discharge curves of lithium/vanadium diselenide cells as a function of current density. (Whittingham, ref. 71.)

Fig. 6. Cycling behavior of a lithium/vanadium diselenide cell. (Whittingham, ref. 71.)

The specific energy of the VSe_2 cathode with 1 Li/VSe_2 capacity at 2.0 V is 248 W h/kg. Although this energy density is fairly low in comparison with TiS_2, this material may be of special interest because of the flat cell voltage and the high Li reversibility at high rates.

V_2S_5. Recently, Jacobson and coworkers [72] from Exxon Corporation have reported that amorphous V_2S_5, obtained by the controlled thermal decomposition of $(NH_4)_3 VS_4$, exhibited rather superior performance in

secondary Li cells. The first discharge at 0.5 mA/cm^2, of cells containing dioxolane/LiClO$_4$ electrolyte, resulted in a capacity of 2.4 e$^-$/V. The mean discharge voltage was 1.96 V which, together with the high capacity, gives a gravimetric energy density of 950 W h/kg. Increasing the current density to 2.5 mA/cm^2 reduced the capacity in the first discharge only to 2.12 e$^-$/V, showing the high rate capability of the cathode. On recharge to 2.8 V, 80% of the discharge capacity was recovered in the first charge (Fig. 7). With repeated cycling performed at 0.5 mA/cm^2, however, the capacity decreased gradually. Thus on cycles 10, 20, and 30 the capacities were 41, 35, and 33% of the initial capacity. However, it was found that the fall in capacity was accompanied by pronounced changes in the voltage/composition profiles. Thus, the mean cell voltage increased from 1.98 V in the first discharge to 2.28 V in the 30th discharge. Apparently the initial V$_2$S$_5$ was converted into another phase, probably to amorphous VS$_2$. A series of polarization curves at current densities from 0.5 to 8 mA/cm^2 obtained after the 30th cycle, indicated good reversibility for the cathode. The specific energy at the 30th cycle corresponds to 300 W h/kg; still quite attractive. Another attractive feature of this material is that its synthesis is accomplished rather easily.

It is apparent that amorphous metal sulfides constitute an interesting class of compounds which merits further research and developments to fully explore their potential as cathodes for secondary Li cells.
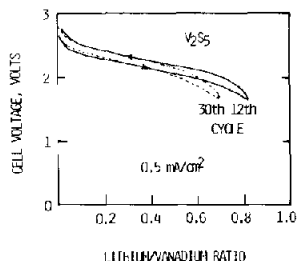

Fig. 7. Cycle data for a Li/LiClO$_4$–dioxolane/V$_2$S$_5$ cell. (Jacobson et al., ref 72.)

CrS_2 and $CrSe_2$. CrS$_2$ is thermally unstable and must be prepared as Li-CrS$_2$ (Van Laar et al. [73]). Although Li can be removed from LiCrS$_2$ electrochemically, only about 20 - 30% is removed at significant current densities, $i.e.$, $\geqslant$ 1 mA/cm^2 (Whittingham [40]). Part of the problem is the higher potentials required for Li removal causing oxidation of the organic solvents. Apparently detailed investigations of this cathode have been limited by the lack of suitable electrolyte systems.

No electrochemical study of CrSe$_2$ had been reported.

1.1.3. Mixed metal disulfides

A series of disulfides having the nominal atom composition $M_xN_{1-x}S_2$, where M is selected from the group consisting of Mn, Fe, Ni, and Co and

mixtures thereof, and N is selected from the group consisting of V and Cr and mixtures thereof, was investigated by Murphy and Disalvo at Bell Laboratories [45, 46]. Compounds on which electrochemical data have been reported are discussed below.

$Fe_{0.25}V_{0.75}S_2$. Cycling studies were carried out with cathodes of very low loading. At current densities less than 0.5 mA/cm^2, 100% cathode utilization (1 Li/host) with a mid-discharge potential of 2.2 V was possible in the first discharge. Utilization on the fifteenth cycle was 90%. This cell has a slightly higher theoretical specific energy (i.e., 510 W h/kg than the Li/TiS$_2$ cell. However, rate-capacity behavior and rechargeability in practical cells have yet to be demonstrated.

$Fe_{0.5}V_{0.5}S_2$. The performance of this cathode was much poorer than that of $Fe_{0.25}V_{0.75}S_2$. Apparently, this material does not merit further consideration.

$V_{0.25}Cr_{0.75}S_2$. At current densities < 0.4 mA/cm^2, utilization in the first discharge was 0.65 Li/host at very low cathode loadings. This utilization fell with cycling, diminishing to ~ 0.57 Li/host at the fifth cycle. Although rate-capacity behavior and rechargeability have not been demonstrated in practical cells, the system may merit further attention because of the very flat discharge at the relatively high voltage of 2.6. This is particularly attractive technologically. At a 0.65 Li/host utilization the specific energy would be 375 W h/kg.

$Cr_{0.5}V_{0.5}S_2$. Although this material constituted one of the members of the mixed metal disulfides discovered by Murphy and coworkers [46], its electrochemical performance has been evaluated only recently at EIC Corporation by Holleck et al. [74].

Cells were cycled with cathodes having capacity densities of 17.5 mA h/cm^2 (based on 1 Li/MS$_2$) so that the data represent the cycling of practical cathodes. Cells were cycled at C/10 rates (1.75 mA/cm^2). A plot of cathode utilization vs. cycle number is shown in Fig. 8. The capacity in the first discharge corresponded to 0.63 e$^-$/host with a mid-discharge potential of 2.44 V. Usually in Li/TiS$_2$ cells having similar cathode loadings, the capacity in the first discharge would be ~ 0.8 e$^-$/TiS$_2$, suggesting that the lower utilization of $Cr_{0.5}V_{0.5}S_2$ in these cells may involve cathode structural factors. Indeed, capacities close to 1 e$^-$/$Cr_{0.5}V_{0.5}S_2$ can be obtained at very low cathode loadings.

The cathode utilization showed a slowly declining trend with cycle number. At the 5th discharge it was ~ 62%. At the 10th discharge it was 54%. At the 20th discharge it was 47%. At the 104th discharge, the capacity was 23%, but when the current was reduced to 30 mA(0.75 mA/cm^2), the rechargeability increased substantially in that the cathode utilization increased to 46% at the 105th discharge. The latter utilization is the same as that in
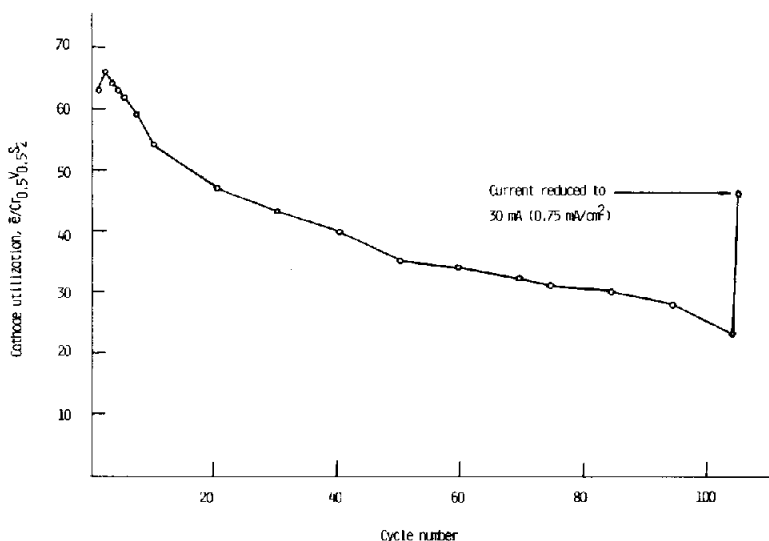
Fig. 8. Cathode utilization *vs.* cycle no. for the $Li/Cr_{0.5}V_{0.5}S_2$ cell. Theoretical cathode capacity = 17.5 mA h/cm^2 based on 1 e$^-$/$Cr_{0.5}V_{0.5}S_2$. Current, $i_d = i_c = 70$ mA except where noted. Current density = 1.75 mA/cm^2. (EIC Data.)

the 20th discharge, suggesting that much of the loss in capacity with cycling results from cathode structural factors.

If the average 0.6 e$^-$ capacity obtained in the first five cycles can be maintained in extended cycling, the $Cr_{0.5}V_{0.5}S_2$ cathode with its relatively higher cell voltage would be quite attractive. The specific energy of the $Li/Cr_{0.5}V_{0.5}S_2$ system with 60% cathode utilization at 2.4 V would be 315 W h/kg. The synthesis of $Cr_{0.5}V_{0.5}S_2$ is relatively easy. Preliminary studies at EIC show that the disulfide has potentially high storage capability at elevated temperatures.

$Cr_{0.33}V_{0.33}Fe_{0.33}S_2$. Only studies utilizing low levels of cathode loadings are available. At current densities < 0.25 mA/cm^2, its initial capacity corresponded to 0.75 Li/host with a mid-discharge potential of 2.45 V. The capacity on the 4th cycle was 0.55 Li/host. Specific energy corresponding to the first discharge is 400 W h/kg. The material may be of interest for further development, particularly in view of the higher cell voltage.

$V_{0.67}Mn_{0.33}S_2$. This material does not appear to be particularly attractive. At low levels of cathode loadings, the initial capacity at < 0.25 mA/cm^2 was 0.5 Li/host with a mid-discharge potential of 2.25 V. The capacity in the 8th cycle was 0.45 Li/host.

1.2. Transition metal trichalcogenides, MX_3

The trichalocogenides which have been investigated as cathode materials for secondary Li cells are; TiS_3, NbS_3, $NbSe_3$ and MoS_3.

TiS₃. The structure of TiS_3 bears some resemblance to those of layered dichalcogenides, showing layer-like characteristics. However, there are two types of sulfur species, a polysulfide radical, S_2^{2-} and a sulfide group, S^{2-}, so that the metal is tetravalent. In the crystal, the van der Waals layer is lined with polysulfide groups [60]. Electrochemical evaluation of TiS_3 in Li cells has been carried out by Holleck *et al.* at EIC [51] and Whittingham *et al.* at Exxon [40, 60].

In the first discharge, up to 3 Li per mole of TiS_3 can be incorporated. The open circuit potential of the cell remains at 2.17 V, almost independent of Li content up to 2 Li, with a gradual fall-off to 1.87 V as a third Li is added. It appears that in the former, the polysulfide bond is broken and a ternary phase is formed. The third Li interacts with the structure in a manner more reminiscent of TiS_2. Only one Li is reversible. Holleck *et al.* have reported more than 100 cycles for a Li/TiS_3 cell with a PC/1M LiClO₄ electrolyte. The cathode utilization in the second discharge was 0.76 e⁻/TiS_3 and in the 100th discharge it was 0.64 e /TiS_3. In the light of these results, it appears that the only likely application for TiS_3 would be in primary Li cells, or cells used a limited number of times.

NbS₃. Niobium trisulfide has a structure analogous to that of TiS_3. Evaluation of the material in Li cells was carried out by Holleck *et al.* at EIC. The electrolyte used was either PC/1M LiAlCl₄, or PC/1M LiClO₄.

The initial discharge showed an extremely flat discharge plateau at 1.8 V. Typically, initial capacities of 2.4 e⁻/NbS_3 were obtained. Only about 55% of this capacity was rechargeable in the first charge, so that in the second discharge the capacity was about 1.4/NbS_3. The second and subsequent discharges proceeded at higher potentials (*i.e.*, a sloping discharge between 2.5 and 1.5 V), indicating cathode structural changes. After 50 cycles, the cathode utilization was still about 1.3 e⁻/NbS_3. With a cathode utilization of ~ 1.3 e⁻/NbS_3 and a mid-discharge potential of 2.0 V, the specific energy of the Li/NbS_3 couple would be 370 W h/kg. This is a rather attractive energy density. However, the cell performance at high cathode loadings, the rate–capacity behavior, low temperature performance, and storageability at high temperature are yet to be assessed.

NbSe₃. The NbSe₃ structure is basically the same as the TiS_3 structure but lacks the simple Se–Se bonding and has a more complex interchain bonding. There is still a van der Waals gap, so that Li intercalation and deintercalation occur during discharge and charge. Electrochemical evaluation of NbSe₃ in Li cells was carried out by Murphy and coworkers at Bell Labs. [75]. The first discharge of NbSe₃ in a Li cell utilizing PC/LiClO₄ at low current densities results in a capacity equivalent to 3 Li/NbSe₃. The first discharge proceeds in 2 distinct steps: a flat plateau region at 1.6 V up to 2 Li/-NbSe₃ and a sloping region to 1.0 V for the third Li. Subsequent cycling of the cathode results in structural changes, so that the discharges occur at higher potentials with a mid-discharge voltage of 1.8 V. The cathode has ex-

hibited very good reversibility. Rates of up to 0.8 mA/cm^2 at cathode loadings of 5.6 mA h/cm^2 (3 Li/NbSe$_3$) have been attempted. Some typical discharge curves according to Murphy *et al.* [75] are shown in Fig. 9. The capacity after > 200 cycles (equivalent to > 100 deep "3 Li" cycles) is still nearly 2 Li per NbSe$_3$ and 75% of the initial capacity. The specific energy of the Li/NbSe$_3$ couple based on the experimental data (2 Li/NbSe$_3$ at 1.8 V) is 280 W h/kg. More significantly, the volumetric energy density for the same cathode utilization would be ~ 1.0 W h/cm^3 (Trumbore, 1979) whereas for TiS$_2$ with 1 e$^-$/TiS$_2$ utilization it would only be 1.2 W h/cm^3. There is no reason to believe that cathode utilizations higher than that already achieved, *i.e.*, the maximum 3 Li/NbSe$_3$ [76], are not possible.
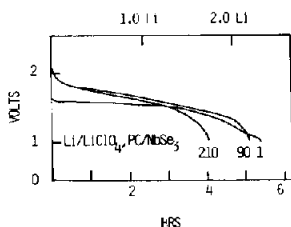

Fig. 9. Discharge behavior of Li/NbSe$_3$ cells (Murphy *et al.*, ref. 75).

Further evaluation with respect to rate/capacity behavior, low temperature performance, cycling characteristics at cathode loadings comparable with practical cells, and cathode storageability at higher temperatures, is yet to be carried out. The synthesis procedure for NbSe$_3$ is comparable in difficulty with that of TiS$_2$. Both NbSe$_3$ and its lithiated products are electronically conducting, as in the case of TiS$_2$. Because of these many attractive features, especially the volumetric energy density, Li/NbSe$_3$ secondary cells may find special practical applications [76].

MoS$_3$. Recently, an amorphous composition of MoS$_3$ was prepared at Exxon by Jacobson *et al.* [77]. Preliminary electrochemical data are promising. Cells were cycled at 0.5 mA/cm^2, utilizing cathodes with and without a graphite conductive diluent. The electrolyte was dioxolane/LiClO$_4$. Cells with, and without, graphite diluent performed similarly. Initial discharge corresponded to capacities of 3.5 to 3.8 e$^-$/MoS$_3$. The discharge shows a flat voltage profile at ~ 1.9 V. After the first discharge, there was a loss in capacity corresponding to 10 - 20% of the initial discharge capacity. On subsequent cycling this capacity was maintained for several cycles.

Although only preliminary data are available to date, the material is promising enough to warrant further investigation. The specific energy calculated from the experimental data (3 e$^-$/MoS$_3$ at 1.9 V) is 715 W h/kg, a very high value indeed.

1.3. Transition metal tetrachalcogenides

$NbSe_{4+x}$. Murphy and coworkers [78] investigated $NbSe_4$ and $NbSe_{4.5}$ as reversible cathodes for Li cells.

The first discharge of $NbSe_4$ results in a capacity of 3.8 e^-/mole. The discharge shows a flat voltage profile at ~ 1.8 V. At relatively low current densities, over 96% of the capacity is recharged in the first charge. However, the capacity declined with repeated cycling falling to ~ 50% in the 10th cycle and ~ 35% in the 25th cycle. Niobium tetraselenide is a poor electronic conductor and the cathode additive of either graphite or the electronic conductor $NbSe_3$ was necessary to fabricate workable cathodes.

Cells employing $NbSe_{4.5}$ failed sooner than those containing $NbSe_4$. Although part of the problem was attributable to poor cathode structure, the overall performance of $NbSe_{4.5}$ was inferior to that of $NbSe_4$. Neither of these selenides merits further consideration.

1.4. Layered transition metal phosphorus trisulfides

A class of layered transition metal phosphorus trichalcogenides, represented by the general formula MPX_3, where M = Fe or Ni and X = S or Se, has been synthesized and evaluated as cathodes for secondary Li cells by Thompson et al. at Exxon in the U.S.A. [79, 80] and at Marcoussis in France by LeMehaute et al. [81, 82]. These compounds have structures very similar to that of TiS_2. The transition metal atoms and the P–P pairs occupy sites that Ti would fill in the TiS_2 structure.

Most studies have been carried out with $NiPS_3$. Reaction of $NiPS_3$ with n-BuLi resulted in an uptake of 4.5 Li per mole of $NiPS_3$ [79]. Electrochemically, however, only 3.5 Li could be incorporated in the initial discharge [79]. The discharge proceeds with a constant cell potential of 1.8 V until three Li have been incorporated and then continues with a sloping potential region to 1.5 V for the remaining 0.5 Li. Thompson et al. have cycled cells 300 times to a depth of 30% of the initial discharge, i.e., ~ 1 e^-/-$NiPS_3$. With $FePS_3$ as cathodes, Thompson et al. have cycled cells 20 times to a depth of 1.5 Li/$FePS_3$. Apparently some structural changes do occur after the initial discharge, since the discharge potentials move to higher values.

A different picture of the electrochemical behavior of $NiPS_3$ appears from the work of the French group [82]. They also obtained a capacity > 3 e^-/$NiPS_3$ in the initial discharge. However, the discharge apparently proceeded with voltage steps, indicating phase changes in the cathode after lithiations of 0.5 Li and 1.5 Li. Their work suggests that at Li compositions > 1.5/$NiPS_3$, a heterogeneous phase exists with the formation of Li_2S. Thus, decomposition of the cathode apparently occurs at high lithiation. This study suggests that the maximum reversible capacity of $NiPS_3$ would be about 1.5 Li/$NiPS_3$.

At reasonable current densities, i.e., > 1.0 mA/cm^2, one can expect a reversible capacity of ~ 1 e^-/$NiPS_3$ with a cell voltage of ~ 1.8 V. This

would translate to a specific energy for Li/NiPS$_3$ cells of 250 W h/kg. The cycling data available to date suggest that the material may undergo irreversible changes during deep discharges. The synthesis of MPS$_3$ compounds involves tedious high temperature procedures. For these reasons, MPS$_3$ compounds do not appear to be attractive for high energy density cells.

1.5. Layered metal oxyhalides

The layered oxyhalides, FeOCl [83 - 85] and UO$_2$F$_2$ [86], have been recently evaluated as cathodes for secondary Li cells.

FeOCl. Although structural considerations would suggest a capacity of 1 Li/FeOCl, only 0.5 Li could be incorporated electrochemically. The discharge proceeds with a constant cell voltage of ~ 2.0 before a rapid potential drop to < 1.5 V at a composition of ~ 0.5 Li/FeOCl. Reaction of n-BuLi with FeOCl showed a tendency for the material to decompose at Li contents > 0.5 in Li$_x$FeOCl. According to Whittingham, the rechargeability of the Li/FeOCl cell is much inferior to that of the Li/TiS$_2$ cell. The known chemistry of FeOCl [85] suggests that the cathode would decompose in a Li cell during prolonged storage to form LiCl and other products. The Li reactions of the related oxychlorides, VOCl and CrOCl, are irreversible [87].

UO$_2$F$_2$. This fluoride has a structure superficially similar to that of TiS$_2$, comprising layers made up of uranium atoms surrounded by a distorted octahedron of fluorine; the oxygen of the UO$_2$$^{2+}$ ions is found in the faces of these octahedra bounding the van der Waals layer [40].

Reaction of UO$_2$F$_2$ with n-BuLi has resulted in an uptake of 2 Li/UO$_2$-F$_2$ [86]. The Li/UO$_2$F$_2$ cell utilizing THF/PC/LiClO$_4$ electrolyte has an OCV of 3.0 V, but upon discharging at 0.1 mA/cm^2, the cell rapidly polarized to ~ 1.25 V, at which potential the discharge proceeded. The charge proceeded at a constant voltage of ~ 3.2 V, showing poor voltage efficiency for cycling. The discharge potential could be raised to ~ 1.5 V by starting with a cathode in the discharged state as Li$_2$UO$_2$F$_2$ (from n-BuLi reaction) and activating the cathode by an initial charge. No data are available on the cycle life of the cathode. In spite of this, the relatively high equivalent weight (eq.wt. = 158) coupled with the low cell potentials and the poor voltage efficiency of cycling make this cathode very unattractive.

2. Metal chalcogenides with complex structures

Several metal chalcogenides having complex crystal structures have been investigated as cathode materials for secondary Li cells. The materials which are discussed in this section are: (i) channel-type chalcogenides, Mo$_3$-X$_4$, X = S or Se; (ii) the sulfospinels, M$_1$^{II}M$_2$^{III}S$_4$ where M$_1$ = Cu, Fe, Co, Ni, Mn, Zn, and M$_2$ = Ti, V, Cr, Fe, Co, and Ni; (iii) the iron sulfides, M$_x$FeS$_2$, where M = K for x = 1 and M = Sr and Ba for x = 0.5; (iv) the copper sulfides, CuS, CuFeS$_2$ and related compounds, and (v) Bi$_2$S$_3$.

Mo$_3$X$_4$; X = S or Se. These compounds were evaluated by Schollhorn and coworkers in Germany [88]. These chalcogenides, possessing three-dimensional network structures, undergo reversible cathode reactions in Li cells in a topochemical fashion.

Initial discharge of Mo$_3$S$_4$ in a Li cell utilizing DME/LiClO$_4$ results in a capacity of 1.8 e$^-$/Mo$_3$S$_4$. The discharge proceeds in 2 steps; the first step, involving 0.5 Li, occurred at ~ 2 V, and the second step, involving 1.3 Li, occurred at ~ 1.8 V. The cell is rechargeable with ~ 75% reoxidation efficiency in the initial cycles and close to 100% reoxidation efficiency after 10 cycles. Only low rate cycling (~ 300 μA/cm^2) has been reported. With a cathode utilization of 1.8 e$^-$/Mo$_3$S$_4$ at 1.8 V, the specific energy of the Li/Mo$_3$S$_4$ couple would be 218 W h/kg.

According to Schollhorn *et al.*, preliminary galvanostatic experiments with Mo$_3$Se$_4$ indicated a behavior very similar to that of Mo$_3$S$_4$ electrodes. They have also reported in the same paper that Nb$_3$S$_4$ and Nb$_3$Se$_4$ undergo reactions similar to the molybdenum chalcogenides, with a charge transfer value of ~ 0.8 e$^-$/Nb$_3$X$_4$. These materials would not be attractive from an energy density standpoint.

2.1. Sulfospinels, $M_1{}^{II}M_2{}^{III}X_4$

This class of compounds has been investigated by Eisenberg at the Electrochimica Corporation. In a patent [89], several materials have been claimed as possible cathode materials. These compounds are CuCo$_2$S$_4$, CoTi$_2$S$_4$, CoFe$_2$S$_4$, CoCr$_2$S$_4$, MoTi$_2$S$_4$, VTi$_2$S$_4$, Co$_3$S$_4$, CuCr$_2$S$_4$, and NiCr$_2$-S$_4$. However, the rechargeability behavior of only three materials, namely, CoFe$_2$S$_4$, Co$_3$S$_4$, and CuCo$_2$S$_4$, is reported. Cycling studies with these materials were carried out, apparently with "practical" cathodes [90, 91].

THF/DME/LiClO$_4$ electrolyte cells with CoFe$_2$S$_4$ and Co$_3$S$_4$ exhibited high OCVs, in the range of 2.8 - 2.9 V. However, they discharge at rather low voltages. For example, at 1.0 mA/cm^2, the discharge of a Li/CoFe$_2$S$_4$ cell proceeds at 1.5 - 1.2 V and the discharge of Li/Co$_3$S$_4$ proceeds at 1.1 - 0.8 V. Moreover, charging of these materials involved relatively high voltages in the range 3.1 - 3.4 V. The presently avilable data do not suggest practical uses for these two materials.

Better performances have been shown by CuCo$_2$S$_4$. This material apparently is capable of cycling 2 Li/mole of CuCo$_2$S$_4$ reversibly. However, the discharge potentials after a capacity of 0.8 e$^-$/CuCo$_2$S$_4$ occur between 1.5 and 1.1 V. The material apparently exhibited good rechargeability for cycling between 2.4 and 1.1 V, with a cathode utilization of 2 e$^-$/CuCoS$_4$. The rate capability of the material is also good. What appears from the published data, however, is that reasonably attractive voltages (> 1.5 V) are possible only up to a capacity of 0.8/CuCo$_2$S$_4$, which does not make this material very attractive. A general disadvantage of low potential cathodes would be that repeated cycling of cells to potentials to, or below, 1 V could lead to irreversible reduction of the solvents, resulting in poor Li cycling efficiency.

M_xFeS_2, *where M = K for* x = *1 and M = Sr and Ba for* x = *0.5.* Jacobson and coworkers [92, 93] have shown that the compounds, $KFeS_2$, $Sr_{0.5}$-FeS_2, and $Ba_{0.5}FeS_2$ are electrochemically active, reversible cathode materials suitable for nonaqueous Li cells. This class of materials is structurally characterized by infinite chains of edge-shared iron–sulfur tetrahedra with the large alkali or alkaline earth metal ions in eight coordinate sites between the chains. A cell with crystalline $KFeS_2$ and no added graphite was discharged at 0.5 mA/cm^2 to a lower cutoff voltage of 1.3 V and then recharged at the same rate to 2.72 V. The total capacity in the first discharge was 0.6 Li per $KFeS_2$. The initial cell voltage of close to 2.6 V falls rapidly to 1.56 V and then slowly to the 1.3 V lower cutoff. On recharge, the voltage rises smoothly to 2.2 V and then steeply to the upper cutoff. At this stage, the system is not completely reversible, only about 50% being recovered on this first cycle. However, the behavior on the second and subsequent discharges was markedly different. The voltage initially dropped to 2.06 V, but this fell smoothly over the whole range and a greater proportion of the discharge capacity was recovered as cycling continued. Thus, on cycle 14 the recharge capacity is 97.5% of the discharge and the overall utilization is 0.65 Li. The discharge profiles with and without graphite were similar, though with graphite added a greater initial capacity was obtained, probably due to increased electronic conductivity.

The behavior of both $Ba_{0.5}FeS_2$ and $Sr_{0.5}FeS_2$ was similar to that of $KFeS_2$. The first discharges were flat at voltages close to 1.5. Subsequent discharges are smoothly varying from above 2.0 V to the lower 1.30 V cutoff, and the systems show an increase in reversible capacity over the first few cycles. The maximum utilizations obtained on cycling were 0.6 Li/$Ba_{0.5}$-FeS_2 and 0.7 Li/$Sr_{0.5}FeS_2$.

The synthesis of these materials is accomplished using high temperature (800 - 900 °C) procedures. The cell voltages are relatively low, *i.e.*, < 2.0 V. High rate cycling was apparently not possible due to the relatively lower Li diffusion in the solid state. The specific energy of $KFeS_2$ with 0.65 Li utilization at 1.9 V is only 213 W h/kg.

Copper sulfide, CuS. A primary Li/CuS battery has been known for some time [94, 95], and a specific energy of 110 W h/lb has been achieved for D-size cells. Recently, it has been shown at EIC by Brummer *et al.* [32] that Li/CuS cells are rechargeable. One cathode was cycled over 300 times in a cell utilizing THF/LiAsF$_6$ electrolyte. The cathode had a theoretical capacity of 7 mA h/cm^2, based on 2 e$^-$/CuS. A cathode utilization of 1.6 e$^-$/CuS was obtained in the first few cycles. This decreased to ~ 0.8 e$^-$/CuS after ~ 40 cycles. A typical discharge/charge curve is shown in Fig. 10. The average cell voltage is 1.7. With an average cathode utilization of 0.8 e$^-$/CuS at 1.7 V, the specific energy of the Li/CuS couple is 360 W h/cm^3, which is similar to the semi-theoretical value for the Li/TiS$_2$ couple.

Although more work dealing with low temperature performance, rate-capacity behavior, and rechargeability in cells with practical cathode loading

needs to be done, CuS is a material which deserves further attention because of its relatively low cost and its ready availability. A major drawback would be the extremely low electronic conductivity of CuS.
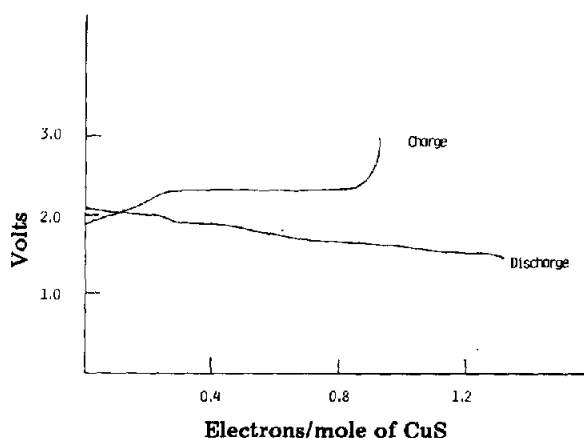

Fig. 10. Charge/discharge curves of the Li/CuS cell in the first cycle. $i_d = i_c = 1.0$ mA/cm^2 (EIC Data, Ref. 32).

2.2 Chalcopyrites

These are copper ores having the nominal composition, CuFeS$_2$. The electrochemical activity of these compounds was discovered by Eisenberg at the Electrochimica Corporation [96].

A copper concentrate having the composition, 27% Cu, 21% Fe, 24% S (*i.e.*, Cu$_{1.12}$Fe$_1$S$_{1.97}$), and the remainder silica and other inert subtrates, showed the following performance in a Li cell. The cell utilized as electrolyte 2M LiClO$_4$ in a mixture of 70 vol % THF and 30 vol % DME. A 2.5 cm × 2.5 cm cathode was fabricated with 15% graphite as a conductive diluent and 7% Teflon binder. In the first discharge, the cell delivered a capacity equivalent to 220 mA h per gram of ore between 2.1 and 1.1 volts. This capacity is equivalent to ~ 1.5 e$^-$/Cu$_{1.12}$FeS$_{1.97}$. The cell was charged from 1.5 to 2.4 V using a 10% excess capacity input. It was cycled 18 times.

Although these materials are attractive with respect to cost and availability, the cell voltages are rather low. Very little data are available on rate/capacity behavior, rechargeability, and low temperature performance. Other ore compositions such as Cu$_1$Fe$_{0.63}$S$_{1.1}$ also behaved similarly.

CoS$_2$ *and* FeS$_2$. These pyrite sulfides were evaluated by Eisenberg [97]. Only preliminary data are available. Cell voltages of 1.5 - 2.0 were obtained at current densities of 0.5 - 1.0 mA/cm^2. In complete cells of spiral construction, capacities of 140 - 250 mA h/g of active material were obtained at these current densities. Typical charging efficiencies for the initial 10 cycles

were 70 - 80%. As with the chalcopyrites, the major limitation of these materials is the rather low cell voltages. Apparently, the cathode rate capabilities are also quite limited.

2.3. Sulfides of main group elements

Bi_2S_3. Besenhard [98] investigated the Group V sulfides As_2S_3, Sb_2S_3, and Bi_2S_3 as cathode materials for Li cells. They can be discharged according to the reaction

$$M_2S_3 + 6Li \longrightarrow 3Li_2S + 2M. \tag{15}$$
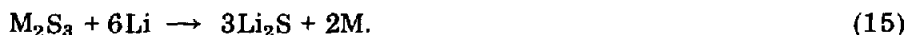
The reaction of Bi_2S_3 with Li was found to be reversible in normal temperature cells utilizing $PC/LiAlCl_4$ electrolytes at low rates of the order of 200 $\mu A/cm^2$. The discharge proceeded with discrete voltage steps. A capacity of 6 e^-/Bi_2S_3 was obtained between 2.0 and 1.0 V. Further capacity, probably corresponding to alloying of Li with Bi, is obtained at $\sim$ 0.80 V. The recharge efficiency of the discharge reaction to 1.0 V at low rates was only $\sim$ 60%. Usually, discharge reactions involving extensive bond breaking, as in the present case, are only poorly reversible at normal temperatures. The recharge efficiency of only $\sim$ 60%, even at the low current densities of 200 $\mu A/cm^2$, is probably indicative of this.

3. Metal oxides with channel type structures as cathodes

A large number of metal oxides with rutile and perovskite-related structures has been investigated as cathodes for secondary Li cells. A review describing the structural aspects of these materials has appeared recently [37].

Murphy and coworkers [99] evaluated a large number of rutile-related metal dioxides, in an attempt to correlate crystal and electronic structural relationships with electrochemical activity in Li cells. Fairly detailed cycling characeristics of three of these dioxides, RuO_2, WO_2, and MoO_2 have been reported by these authors. Murphy *et al.* also investigated the usefulness of the vanadium oxides, V_2O_5, V_6O_{13}, and VO_2 (B). Other oxides which have been evaluated by various workers are MoO_3 and the chromium oxides, Cr_2O_5, Cr_3O_8, and Seloxcette. The latter is a commercially available $CrO_x/-$ graphite preparation.

3.1. The rutile-related metal dioxides

Typical cycling curves, according to Murphy *et al.* [99], for cells utilizing RuO_2, WO_2 and MoO_2, are shown in Fig. 11. Iridium dioxide exhibited behavior apparently similar to that of RuO_2. The e.m.f. of the Li/Li_xMO_2 couples, where M = W, Mo, and Os, was only $\sim$ 1.5 V, as opposed to $\sim$ 2.1 V for cells with RuO_2 and IrO_2.

The discharge of WO_2 and MoO_2 proceeded with distinct breaks in the voltage/time curves, indicating rather complex discharge reactions. These cells have very poor cell voltages. The voltages of RuO_2, and apparently of

OsO_2 cells, were relatively constant at $\sim$ 2.0 V as a function of state of discharge, suggestive of a two phase system. The capacity of all the Li/Li_xMO_2 cells gradually diminished with cycling, even at the low rates employed in these studies. It was suggested by Murphy that a slow disproportionation of the initial discharge product, Li_xMO_2, to thermodynamically more favored products occurs with cycling, causing irreversibility in these types of cathodes. These data suggest that the rutile-related dioxides are probably not suitable as cathodes for practical secondary Li cells.
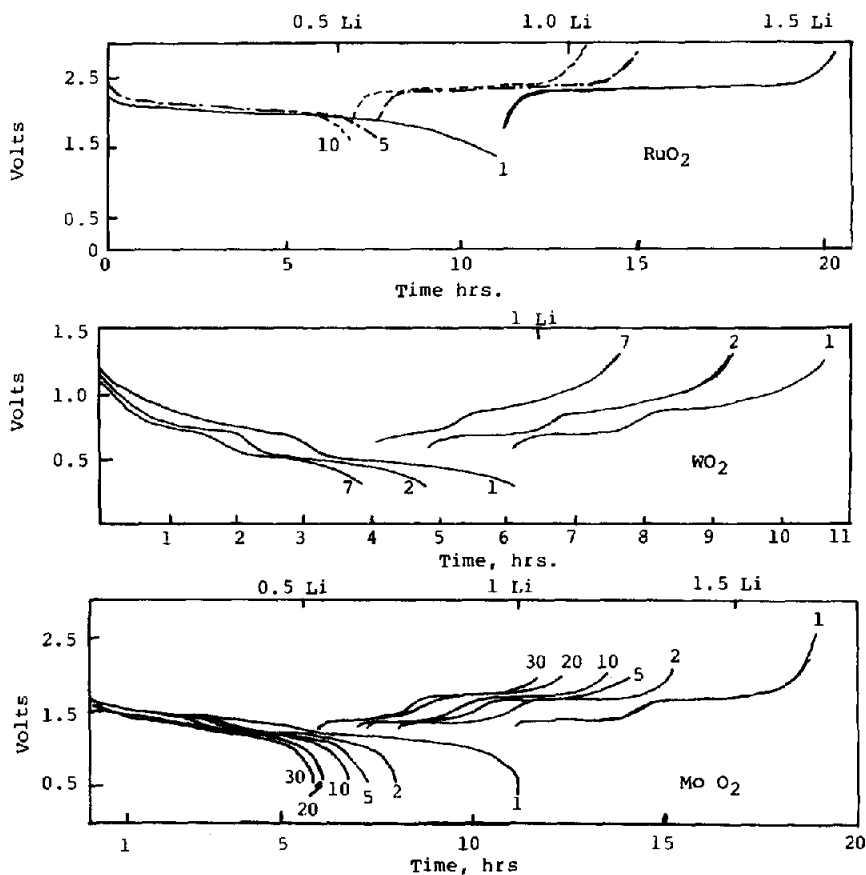

Fig. 11. Cycling curves of rutile related oxides with 1 M $LiClO_4$ in propylene carbonate. Numbers on curves indicate cycle number (Murphy *et al.*, ref. 99).

3.2. Other three-dimensional oxides

3.2.1. *Vanadium oxides.* The vanadium oxides, V_2O_5, V_6O_{13}, and VO_2 (B), comprise a class of framework compounds consisting of shear structures derived from the ReO_3 lattice [37]. The parent structure contains an

extended network of channels intersecting in three mutually perpendicular directions. These channels may be visualized as rising from the sharing of square faces of individual, vacant cavities.

An idealized V_2O_5 structure may be derived from an ReO_3 lattice by removing oxygens from every second (200) plane and closing the structure along the shear vector 1/2(100). The resulting shear structure consists of distorted VO_6 octahedra joined by edge sharing among themselves along (001) into single zig-zag chains linked together by corner sharing to form single sheets. These sheets are joined by means of additional corner sharing into a three-dimensional lattice. The resulting structure contains asymmetric V=O---V units.

The V_6O_{13} lattice may be regarded as a shear structure of V_2O_5. This structure contains distorted VO_6 octahedra joined, by extensive edge sharing, into both single and double zig-zag chains running parallel to (010). Both the single and double sheets are linked by additional edge sharing into single and double sheets, respectively, both lying parallel to the (100) plane. The sheets are interleaved and joined together by corner sharing to form a three-dimensional lattice. This structure contains tricapped cavities joined through shared square faces. The asymmetric V=O---V linkages are absent in the structure.

The metastable VO_2 (B) has a structure related to those of V_2O_5 and V_6O_{13}. The structure may be visualized simply as that obtained by removing the sheets of single chains from the V_6O_{13} structure.

V_2O_5. This oxide has been extensively studied as a cathode for primary Li cells. The rechargeability of the V_2O_5 cathode was shown by Walk and co-workers [100]. The Li/V_2O_5 cell utilizing $PC/LiClO_4$ has an OCV of ~ 3.5. The discharge takes place in discrete potential steps and proceeds to a depth of more than one Faraday/mole of V_2O_5. If the discharge is limited to one Faraday/mole, the reaction is reversible. In "prototype cells" using rates of 1.0 mA/cm^2 for discharge and 0.5 mA/cm^2 for charge, nearly 400 cycles were achieved at a 20% depth of discharge (0.2 e$^-$/V_2O_5).

Although the cells have high cell voltages (> 2.8) and V_2O_5 is relatively inexpensive and readily available, the material apparently has two major limitations: (i) rechargeability is quite sensitive to over-discharge; (ii) cathode utilization falls off quite drastically at rates above 1.0 mA/cm^2.

Studies by Murphy [37] seem to suggest that the irreversibility of the V_2O_5 cathode for Li contents greater than 1 Li/V_2O_5 results from the rupture of the V-O bond in the V_2O_5 polyhedra. Other limitations in the use of V_2O_5, even at a cathode utilization limit of 1 Li/V_2O_5, are: (i) oxidation of organic solvents at the high voltages necessary for charging; (ii) the finite solubility of V_2O_5 in organic solvents; (iii) its low electronic conductivity.

V_6O_{13}. Two types of V_6O_{13} can be prepared depending upon the synthetic procedure [101]. Stoichiometric V_6O_{13}, ($VO_{2.17}$), can be prepared

by the reduction of V_2O_5 with the stoichiometric amount of V at 650 °C. Non-stoichiometric V_6O_{13} ($VO_{2.19}$ to $VO_{2.21}$) is obtained by the thermal decomposition of NH_4VO_3. The stoichiometric V_6O_{13} usually has particle sizes of 10 - 50 μm, whereas the non-stoichiometric material is composed of 1 - 5 μm particles. The extent of Li uptake by these materials in the reaction with n-BuLi suggests that they may differ structurally as well: thus, stoichiometric V_6O_{13} incorporates a maximum of 4 Li/V_6O_{13}. Non-stoichiometric material affords $Li_8V_6O_{13}$. Differences in performance are also observed in electrochemical cells.

Murphy [101] has evaluated the two V_6O_{13} materials in Li cells utilizing $PC/LiAsF_6$ electrolyte with cathodes of extremely low capacity/ unit area. Typical cycling curves according to Murphy are shown in Figs. 12 and 13.
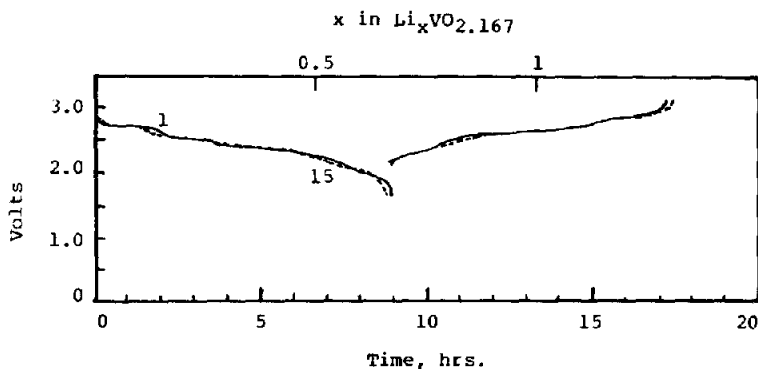

Fig. 12. Cycle data for a cell containing 8.5 mg of 10 - 50 μm V_6O_{13}. The electrolyte was $LiAsF_6$ in propylene carbonate. The current was 0.2 mA. Cycle numbers are indicated. (Murphy *et al.*, ref. 101.)
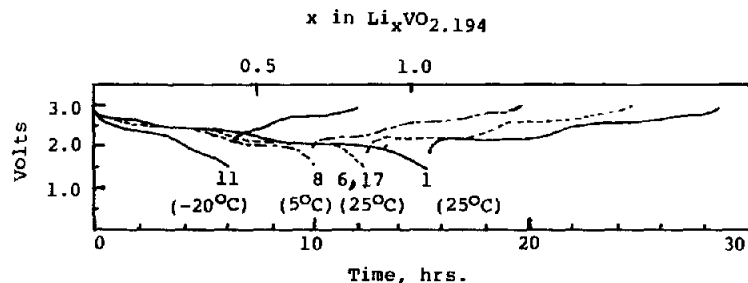

Fig. 13. Cycle data for a cell containing 19.4 mg of 1 - 5 μm V_6O_{13}. The current was 0.2 mA. The capacity decreases at lower temperatures and recovers when the cell is returned to room temperature. Cycle numbers are indicated. (Murphy *et al.*, ref. 101.)

Stoichiometric V_6O_{13} exhibits a capacity of 0.65 e^-/V in the first discharge with a mid-discharge potential of $\sim$ 2.3. The discharge and charge

proceed with distinct breaks in cell voltages as a function of state of charge, suggesting complexities in the Li/V_6O_{13} phase diagram. The cell exhibited virtually no capacity loss with cycling.

Non-stoichiometric V_6O_{13} exhibits a capacity of 1 e^-/V in the first discharge with the additional capacity occurring as a plateau at $\sim$ 2.2 V. Only 80% of this capacity is recharged in the first charge. According to Murphy's data, the capacity showed only minor losses in subsequent cycling. The average rechargeable capacity appears to be $\sim$ 0.7 e^-/V at low cathode loadings.

The electrochemical performance of both types of V_6O_{13} has been studied at EIC by Abraham $et\ al.$ [102] with cathodes having theoretical capacities of $\geqslant$ 10 mA h/cm^2. The cells utilized 2Me-THF/$LiAsF_6$ (1.5M) electrolyte. The pressed cathodes contained 20 wt.% C and 10 wt.% Teflon binder. A plot of cathode utilization $vs.$ cycle number for a typical cell utilizing stoichiometric V_6O_{13} is shown in Fig. 14. At a discharge rate of 1.0 mA/cm^2, initial cathode utilization was $\sim$ 0.55 e^-/V. With current densities of 1.0 mA/cm^2 for both discharge and charge, the cathode utilization remained practically constant. The stoichiometric V_6O_{13} cathode was cycled 110 times with an average capacity of 0.52 e^-/V. Based on our experimental data, the specific energy of Li/V_6O_{13} cells utilizing the stoichiometric oxide is 350 W h/kg.
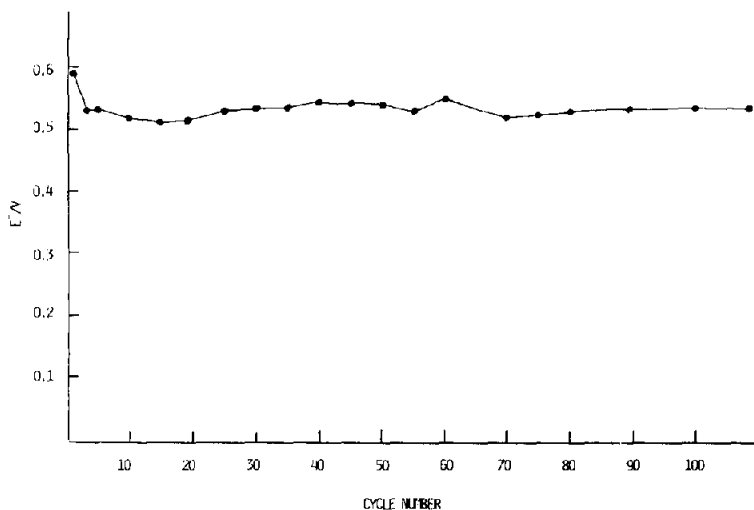

Fig. 14. Plot of cathode utilization (electrons per vanadium, e^-/V) $vs.$ cycle no. for Li/V_6O_{13} cell utilizing stoichiometric V_6O_{13}. The electrolyte was 2 Me-THF/1.5 $LiAsF_6$. Current density = 1 mA/cm^2. Voltage limits were 1.9 for discharge and 3.0 for charge. (EIC Data.)

A preliminary evaluation of the rate/capacity behavior of the stoichiometric oxide was carried out at EIC [102]. For a cathode having a theoretical capacity density of 21 mA h/cm^2 (based on 1 e^-/V), the utilization was

~ 0.55 e$^-$/V at current densities of 0.5, 1.0, and 2.0 mA/cm^2. At 4 mA/cm^2, the utilization was 0.45 e$^-$/V.

A plot of cathode utilization *vs.* cycle number for a high capacity Li/V$_6$O$_{13}$ cell, utilizing the non-stoichiometric oxide at 0.5 mA/cm^2, is shown in Fig. 15. The pressed cathode contained 20 wt.% carbon, and 10 wt.% Teflon binder. The capacity in the first discharge to a cutoff of 1.9 V was ~ 1.0 e$^-$/V, in agreement with Murphy's results. Typically this material, about 15 - 20% of the discharge capacity could not be recharged in the first charge. Also, the cathode utilization declined with cycling, especially in the early cycles. In the cell shown in Fig. 15, the capacity declined to 0.65 e$^-$/V by the 16th cycle. From cycles 17 - 40, the cathode utilization was maintained at 0.65 e$^-$/V. Rechargeability of these cells was found to be extremely sensitive to discharge voltage limits. This is shown in Fig. 16. In this cell, the voltage limits of cycling were 3.0 and 1.9 for the first 15 cycles. The performance of the cell is similar to that shown in Fig. 15. At the 16th discharge, the lower voltage limit was changed to 1.4 and cell performance subsequently declined drastically.
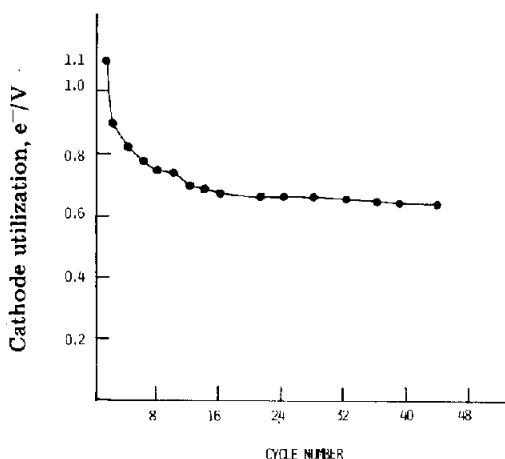

Fig. 15. Cathode utilization (e$^-$/V) *vs.* cycle number for an Li/V$_6$O$_{13}$ cell utilizing non-stoichio metric V$_6$O$_{13}$. Current density = 0.5 mA/cm^2 for both discharge and charge. Voltage limits were 3.0 for charge and 1.9 for discharge. (EIC Data.)

Our data suggest that the sensitivity to overdischarge may be a major deterrent to practical use of these materials. Preliminary data suggest that the performance of the stoichiometric V$_6$O$_{13}$ may also be sensitive to deep discharge. We have also found that, in high capacity cells utilizing both types of oxide, the cathode utilization, even in the first discharge, would be extremely low (< 0.2 e$^-$/V) if there is no carbon present in the cathode. Thus, our data imply serious limitations to the use of these oxides in practical secondary Li cells.
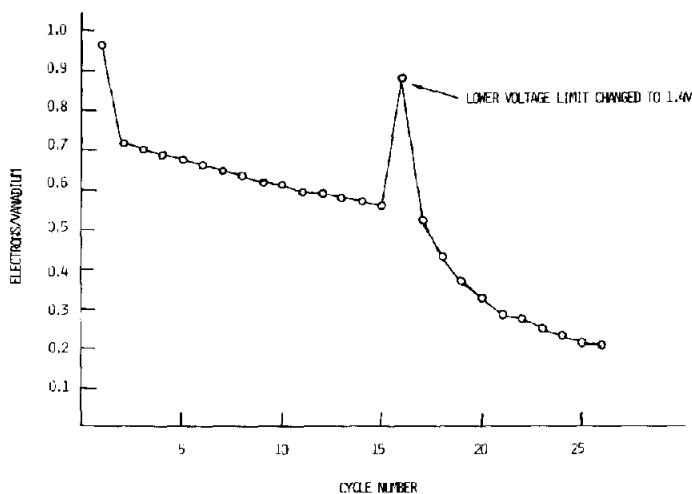
Fig. 16. Cathode utilization *vs.* cycle number for an Li/V_6O_{13} cell utilizing non-stoichio-metric oxide (0.5 mA/cm^2). For cycles 1 - 15 voltage limits were 3.0 and 1.9. For cycles 16 - 26 voltage limits were 3.0 and 1.4. (EIC Data.)

Other vanadium oxides. The metastable VO_2 (B) incorporated ~ 0.5 Li both electrochemically and from n-BuLi [37, 101]. Apparently < 0.5 Li/-VO_2 (B) could be cycled in low capacity cells. V_3O_4 reversibly incorporates 0.33 Li/V above 2.5 V and also exhibits substantial irreversible capacity above 2.0 V. Appreciable capacity was obtained with V_4O_9, *i.e.*, 0.75 Li/V, although these cells exhibited poor rechargeability.

3.2.2. Chromium oxides. Besenhard and Schollhorn [103] investigated the chromium oxides, Cr_2O_5, Cr_3O_8, and CrO_x–graphite, known commercially as Seloxcette.

All the three oxides show fairly identical reduction/oxidation behavior. Figure 17 shows the galvanostatic reduction and reoxidation of Seloxcette, corresponding to a formal Cr/O ratio of $CrO_{2.46}$ in DME (1,2-dimethoxy-ethane)/$LiClO_4$. The first discharge corresponds to a charge transfer of 1.24
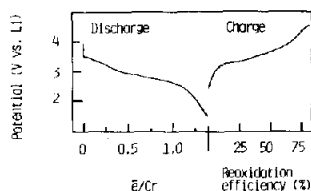

Fig. 17. Charge/discharge cycle of Seloxcette in DME/$LiClO_4$, i = 200 μA/cm^2.

e^-/Cr to 2.0 V. The discharge proceeds from 3.5 V, in a downward sloping fashion, with a mid-discharge potential of $\sim$ 2.8 V. In the current density range $0.1 < i < 1.0$ mA/cm^2, the discharge utilization depended only slightly on current density. However, the reoxidation efficiency was only $\sim$ 75 - 80%, even in low rate galvanostatic cycling. Extended cycling data, or performance of high capacity cells, are not available. The higher charging potentials required may lead to solvent degradation, and thereby limit the use of these cathodes with most electrolyte systems.

The maximum utilization of Cr_2O_5 and Cr_3O_8 pressed powder electrodes containing 35 wt.% graphite was close to 1.4 e^-/Cr. The shape of the Cr_3O_8 discharge characteristics nearly coincided with that of Seloxcette, with a plateau at $\sim$ 3.0 V. This voltage plateau was slightly lower in the case of Cr_2O_5.

These cathodes, potentially, have extremely attractive energy densities. The calculated theoretical specific energy of the Li/Cr_3O_8 couple is 1080 W h/kg, based on the experimental values of 1.4 e^-/Cr utilization and average cell voltage of 3.0. Practical applications would be contingent upon further developmental work. Such work would be justified by the fact that these cells are potentially capable of high capacities at high voltages.

3.2.3. Molybdenum oxide

MoO_3. The usefulness of MoO_3 as a reversible cathode was first discovered by Campanella and Pistoia [104]. Further work on this material as a secondary cathode was performed by Hunger and coworkers [105].

Campanella and coworkers studied cells of the type $Li/LiAlCl_4-BL/-MoO_3,C$, where BL = butyrolactone. The cell had an OCV of 2.8. Pressed cathodes were prepared using 70 wt.% MoO_3 and 30 wt.% graphite. Typical cathodes of 4.3 cm^2/side contained $\sim$ 0.3 g MoO_3. First discharge at 0.5 mA/cm^2 (C/23) or at 1.0 mA/cm^2, resulted in a capacity of 1.32 e^-/MoO_3. At 2 mA/cm^2 the capacity was 1.1 e^-/MoO_3. One cell was cycled 30 times at 1.0 mA/cm^2 between voltage limits of 3.6 and 1.0. The cell capacity decreased with cycling and an average cycling efficiency of $\sim$ 61% was obtained in the 30 cycles.

Hunger and coworkers [105] studied the rechargeability behavior of MoO_3 in more detail. They found that the initial discharge, involving the reaction $2MoO_3 + Li^+ + e^- \longrightarrow LiMO_2O_6$, is not rechargeable. Further discharge of LiM_2O_6, to form Li_2MoO_3, is rechargeable. They have also found that the cathode was extremely sensitive to discharges below $\sim$ 1.5 V. During such discharges irreversible damage of the cathode apparently occurred with subsequent poor rechargeability. This behavior is similar to that which we have observed for V_6O_{13}.

Although MoO_3 potentially has high energy density capabilities, its extreme sensitivity to deep discharge, and the high potentials required for recharging (> 3.0 V) may impose limitations on its use in practical cells.

Recently, Icovi and coworkers reported [106] that Mo oxides of general formula Mo_nO_{3n-1} could be used as rechargeable cathodes. The

oxides investigated were Mo_4O_{11}, Mo_8O_{23} and Mo_9O_{26}. A major problem observed in these oxides was also the structural breakdown upon deep discharge. The e^-/Mo values which allow structure retention in the $Li_xMo_nO_{3n-1}$ ternary phases are lower than that found with MoO_3. The immediate applications of these oxides may be in high capacity primary cells.

These molybdenum oxides, along with two other oxides, $Mo_{17}O_{47}$ and $(Mo_{0.92}V_{0.08})_5O_{14}$, were investigated also by Christian and coworkers [107]. Their results were in general agreement with those of Icovi et $al.$ The molybdenum oxides, in general, show irreversible structural changes upon deep discharge.

3.2.4. Li_xCoO_2. This new cathode system has recently been reported by Mizushima and coworkers [108]. Lithium cells were constructed with Li-CoO_2 as the cathode and $PC/LiBF_4$ as the electrolyte. The cell exhibited very high voltages with OCV's lying in the range 3.9 - 4.7 for $0.07 < x \leqslant 1$ in Li_xCoO_2. Although virtually all the Li in $LiCoO_2$ could be removed electrochemically, reversibility tests were carried out only in the range of compositions between $LiCoO_2$ and $Li_{0.5}CoO_2$. The extremely high cell voltages would preclude the use of most organic electrolytes. A possible application of this material would be in the construction of cells with Li intercalates, for example, $LiTiS_2$, as anodes. The layered rock salt structure of $LiCoO_2$ is adopted by several transition-metal–lithium oxides, $LiMO_2$, including M = V, Cr, Co, Ni, and Fe, and the possibility of obtaining new and useful cathode materials for rechargeable Li cells is indicated.

D. Conclusions

Several soluble cathode materials, notably $CuCl_2$, Br_2, and soluble S, potentially have high energy density, rate, and good rechargeability characteristics. However, a major deterrent to their practical use is the unacceptably high self-discharge rate. One solution to the problem would be to use Li^+ ion-exchange membrane separators.

For the immediate future, the most fruitful approach for the development of practical rechargeable Li cells appears to be the use of insoluble cathodes. Table 4 lists various Li/cathode couples which exhibited semi-theoretical specific energy of about 300 W h/kg or greater, in laboratory cells. In practice one can expect to obtain ~ 25 - 30 percent. of this energy density. Most of these materials have not been investigated beyond the laboratory scale. The most actively pursued material has been TiS_2, particularly by research groups at EIC and Exxon. A few other disulfides, particularly the mixed metal disulfides, are worthy of further development. Copper sulfide appears to be another attractive material.

The amorphous sulfides, notably MoS_3 and V_2S_5, are promising enough to warrant considerable further consideration.

TABLE 4

Energy densities of rechargeable cathodes for Li cells

Cathode material	Li utilization/ mole of cathode material	Energy density W h/kg*,**	Energy density W h/cm³***	Extent of investigation and related comments
ZrS_2	1.0 (possible)	330 (82 - 110)	1.0	No cell studies reported. Crystallographic changes occur from a 1-block to a 3-block structure during Li intercalation. This may suggest poor rechargeability.
TiS_2	1.0	480 (120 - 158)	1.20	Most extensively studied cathode material. Excellent rechargeability and rate capability. D-size cells built at EIC. Energy densities of these D cells were somewhat poorer, due primarily to scale-up problems and the inefficiency of Li cycling.
VSe_2	1.0	248 (62 - 82)		Excellent reversibility; high rate capability. May be useful for special applications because of the flat cell voltages. Scaled-up cells need to be demonstrated.
V_2S_5	4.8 (first discharge) 1.6 (30th discharge)	950 (238 - 313) 300 (75 - 99)	2.80 0.90	Only laboratory cells studied. Initial studies show attractive rate capabilities.
$Fe_{0.25}V_{0.75}S_2$	1.0	510 (128 - 168)	1.40	Only low capacity laboratory cells studied; high rate cycling yet to be demonstrated. Cell voltages are higher than TiS_2 cells.
$Cr_{0.75}V_{0.25}S_2$	0.65	375 (94 - 124)	1.08	Only low capacity laboratory cells studied. Extended cycling and high rate capabilities yet to be demonstrated.
$Cr_{0.5}V_{0.5}S_2$	1.0 (first discharge) 0.60 (high capacity cells)	525 (131 - 173) 315 (79 - 104)	1.40 0.90	Rechargeability demonstrated in high capacity cells. Rate capability not known. Initial data show good storage capability at high temperature. Scaled-up cells yet to be demonstrated.

Cathode		Capacity**		Comments
NbS$_3$	2.4 (first discharge)	—	—	Only laboratory cells studied with low capacity cathodes at low rates. Rechargeability appears to be good in low capacity cells.
	1.3 achieved in 50 cycles	370 (93 - 122)	1.10	
NbSe$_3$	3.0 (first discharge)	410 (102 - 135)	1.60	Excellent rechargeability. Rate capability in high capacity cells is not known. Volumetric energy density is attractive in spite of the relatively low gravimetric energy density.
	2.0 (100th discharge)	280 (70 - 92)	1.00	
MoS$_3$	3.0	717 (180 - 236)	—	Only preliminary data; very promising. Rate capability and rechargeability have to be demonstrated in practical cells.
CuS	0.80	360 (90 - 119)	1.17	Rechargeability demonstrated in laboratory cells; inexpensive. Major drawbacks are lower cell voltage and insulating character of CuS.
Cr$_3$O$_8$	3.8	~1000 (250 - 330)		Only preliminary studies in laboratory cells at low rates have been reported. Further studies seem warranted because of the very high gravimetric energy density.
V$_6$O$_{13}$ (stoichiometric)	3.60	430 (108 - 142)	1.30	Good rechargeability demonstrated in high capacity cell. Moderately high rates possible. Overdischarge may impede cell performance.
V$_6$O$_{13}$ (non-stoichiometric)	6.00 (first discharge)	636 (159 - 210)	1.32	Cathode utilization decreases with cycling to ~ 4.0. Overdischarge causes irreversible damage.
	4.00 (average rechargeable)	440 (110 - 145)		

*Based on capacities found in laboratory cells. Only cathodes showing capacities of about, or greater than, 300 W h/kg are included. Cathodes with ≤ 1.5 V mid-discharge potential are not included.

**The values in parentheses represent the likely practical specific energy; i.e., ~ 25 - 33% of the semi-theoretical.

***Semi-theoretical values.

The vanadium oxide V_6O_{13} appears at first sight to be a particularly attractive material. Its major drawback is that it shows irreversible changes on over-discharge. The known behavior of other oxides suggests this to be a possible drawback with oxides in general. Research aimed at a general understanding of this problem would be useful for further development of oxide cathodes.

Acknowledgement

References

1 R. J. Jasinski, *High Energy Batteries*, Plenum Press, New York, 1967.
2 L. H. Gaines, R. W. Francis, G. H. Newman and B. M. L. Rao, *11th IECEC Conf.*, Stateline, Nevada, 1976, Amer. Inst. Chem. Engineers, New York, 1976.
3 S. Atlung, K. West and T. Jacobsen, *J. Electrochem. Soc., 126* (1979) 1311. See also, S. Atlung, in A. Kozawa, K. V. Kordesch, E. Voss, J. P. Gabano, K. Fueki, H. M. Joseph, H. Ikeda, T. Shirogami, Y. Uetani and H. Ogawa (eds.), *Progress in Batteries and Solar Cells*, Vol. 2, JES Press, Inc., Ohio, U.S.A., 1979.
4 G. Eichinger and J. O. Besenhard, *J. Electroanal. Chem., 72* (1976) 1.
5 J. J. Auborn, A. Heller and K. W. French, *Proc. 25th Power Sources Symp.*, Atlantic City, N. J., 1972, PSC Publications, Redbank, N. J., U.S.A., 1972.
6 J. J. Auborn, K. W. French, S. I. Liebermann, V. K. Shah and A. Heller, *J. Electrochem. Soc., 120* (1973) 1613.
7 J. J. Auborn, K. W. French, S. I. Liebermann, V. K. Shah and A. Heller, *Rep. AD 763 478*, Nat. Tech. Info. Ser., Springfield, Va, U.S.A., 1973.
8 J. J. Auborn, K. W. French, A. Heller and S. Liebermann, *Rep. AD 767 624*, Nat. Tech. Info. Ser., Springfield, Va., U.S.A., 1973.
9 K. M. Abraham and R. M. Mank, *J. Electrochem. Soc., 121* (1974) 315.
10 A. N. Dey, Contract No. DAAB07-74-C-0109, *Final Rep., ERADCOM-74-0104*, Fort Monmouth, N. J., U.S.A., July 1978.
11 S. Gilman, in B. B. Owens and N. Margalit (eds.), *Ambient Temperature Li Batteries*, The Electrochemical Society, Princeton, N. J., U.S.A., PV 80-4, 1980; S. Gilman and W. Wade, Jr., *J. Electrochem. Soc., 127* (1980) 1427.
12 J. G. Weininger and F. W. Secor, *J. Electrochem. Soc., 121* (1974) 315.
13 D. Herbert and J. Ulam, *U.S. Patent 3,043,896* (1962); *German Patent 1,126,464* (1962).
14 R. J. Jasinski, *Electroanal. Chem., 26* (1970) 189.
15 J. E. Chilton, Jr., W. J. Conner, G. M. Cook and A. W. Holsinger, Lockheed Missiles and Space Co., *Final Rep. on AG-33 (615)-1195, AFAPL-TR-64-147*, Ohio, U.S.A., 1964.
16 M. Shaw and D. McClelland, *U.S. Patent 3,393,092* (1968).
17 J. P. Gabano, G. Gerbier and J. F. Laurent, *Proc. 23rd Power Sources Conf.*, Atlantic City, N. J., PSC Publications, Redbank, N. J., U. S. A., 1969.
18 J. P. Gabano, G. Lehman, G. Gerbier and J. F. Laurent, in D. H. Collins (ed.), *Power Sources 3*, Oriel Press, Newcastle upon Tyne, England, 1971.

19 D. P. Boden, H. R. Buhner and V. J. Spera, *Final Rep. Contract DA 28-043-AMC-01394(E)* September, 1966; Rep. AD 639709, Nat. Tech. Info. Ser., Va., U.S.A., 1976.
20 D. P. Boden, H. R. Buhner and V. J. Spera, *Semiannual Rep. Contract DAAB07-67-C-0385*, U.S. ECOM., Fort Monmouth, N. J., U.S.A., February, 1968.
21 H. N. Sieger, A. E. Lyall and R. C. Shair, in D. H. Collins (ed.), *Power Sources 2*, Pergamon Press, London, 1969, p. 267.
22 M. Eisenberg and K. Wong, *Proc. 23rd Power Sources Conf.*, Atlantic City, N. J., PSC Publications, Redbank, N. J., U.S.A., 1969.
23 *French Patent* (1968).
24 H. Lerner and H. N. Sieger, *J. Electrochem. Soc., 117* (1970) 517.
25 *U.S. Patent* (1968).
26 A. N. Dey and B. M. L. Rao, *Rep. AD 825241*, Nat. Tech. Info. Serv., Springfield, Va., U.S.A., 1967.
27 A. N. Dey and B. M. L. Rao, in D. H. Collins (ed.), *Power Sources 2*, Pergamon Press, London, 1969, p. 231.
28 F. W. Dampier and K. W. Spiegler, *Rep. AD 859386*, Nat. Tech. Info. Serv., Springfield, Va., U.S.A., 1969.
29 F. W. Dampier and K. W. Spiegler, *Rep. AD 882890*, Nat. Tech. Info. Serv., Springfield, Va., U.S.A., 1971.
30 M. B. Armand, J. M. Chabagno and M. J. Duclot, in P. Vashishta, J. N. Mundy and G. K. Shenoy (eds.), *Fast Ion Transport in Solids*, Elsevier, North Holland, 1979, p. 131.
31 R. D. Rauh, K. M. Abraham, G. F. Pearson, J. K. Suprenant and S. B. Brummer, *J. Electrochem. Soc., 126* (1979) 523.
32 S. B. Brummer *et al.*, *Final Rep., U.S. Department of Energy, Contract E4-76-C-02-2520*, Washington, D.C., U.S.A., 1979.
33 K. M. Abraham and R. D. Rauh, Abstr. 2, Fall Meeting, Atlanta, Georgia, October 4 - 9, 1977, *The Electrochemical Society Extended Abstracts*, p. 14.
34 M. L. Rao, *U.S. Patent 3,413,154* (1968).
35 J. R. Coleman and M. W. Bates, in D. H. Collins (ed.), *Power Sources 2*, Pergamon Press, London, 1969, p.289.
36 D. Nole and V. Moss, *U.S. Patent 3,532,543* (1970).
37 D. W. Murphy and P. A. Christian, *Science, 205* (1979) 651.
38 B. C. H. Steele, in W. van Gool (ed.), *Fast Ion Transport in Solids*, Elsevier, North Holland, 1973, p. 645.
39 L. Heyne, in W. van Gool (ed.), *Fast Ion Transport in Solids*, Elsevier, North Holland, 1973, p. 123.
40 M. S. Whittingham, *Prog. in Solid State Chem., 12* (1978) 1.
41 W. L. Worrell and A. S. Nagelberg, in *Proc. Symp. and Workshop on Advanced Battery Research and Designs, NTIS*, Springfield, Virginia, 1976, p. 32.
42 D. W. Murphy and F. A. Trumbore, *J. Cryst. Growth, 39* (1977) 185.
43 F. R. Gamble and T. H. Gabelle, in N. B. Hannay (ed.), *Treatise on Solid State Chemistry*, Vol. 3, Plenum Press, New York, 1976.
44 J. O. Besenhard and R. Schollhorn, *J. Power Sources, 1* (1976) 267.
45 D. W. Murphy, Fall Meeting Electrochemical Society, Atlanta, Georgia, 1977; *Mater. Res. Bull., 12* (1977) 825.
46 F. J. Disalvo and D. W. Murphy, *U.S. Patent 4, 159,962* (1979).
47 G. L. Holleck, EIC Corporation, unpublished results.
48 M. B. Dines, *Mater. Res. Bull., 10* (1975) 287.
49 M. S. Whittingham and F. R. Gamble, *Mater. Res. Bull, 10* (1975) 365.
50 G. L. Holleck, F. S. Shuker and S. B. Brummer, *Proc. 10th IECE Conf.*, Newark, Delaware, IEEE, New York, 1975.
51 G. L. Holleck, J. R. Driscoll and F. S. Shuker, *Final Rep., ECOM Contract DAAB07-74-C-0072*, U.S. ECOM, Fort Monmouth, N. J., U.S.A.

52 G. L. Holleck and J. R. Driscoll, *Electrochem. Acta, 22* (1977) 644.

53 B. G. Silbernagel, *Solid State Commun., 17* (1975) 361.

54 S. Basu and W. L. Worrell, in J. D. E. McIntyre, S. Srinavasan and F. G. Will (eds.), *Electrode Materials and Processes for Energy Conversion and Storage,* The Electrochemical Society, Princeton, N. J., U.S.A., PV77-6, 1977.

55 J. O. Besenhard and R. Schollhorn, *Z. Naturforsch., 31B* (1976) 907.

56 A. J. Jacobson, R. R. Chilannelli and M. S. Whittingham, *J. Electrochem. Soc., 12* (1979) 2277.

57 G. L. Holleck, K. M. Abraham and S. B. Brummer, *J. Electrochem. Soc., 126* (1979) 308C.

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

59 M. S. Whittingham, *U.S. Patent 4,004,052* (1973); G.B. Patent, *1,468,416* (1973); Belgian Patent *819,672* (1973).

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

61 M. S. Whittingham, *U.S. Patent 4,049,887* (1976).

62 V. R. Koch, *U.S. Patent 4,118,550* (1978).

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

64 K. M. Abraham, EIC Corporation, unpublished results.

65 M. S. Whittingham, *U.S. Patent 4,007,055* (1977).

66 A. H. Thompson and F. R. Gamble, *U.S. Patent 3,980,761* (1976).

67 W. Biltz and P. Ehrlich, *Z. Anorg. Allg. Chem. 234* (1937) 97.

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

69 M. Lazzari and B. Scrossatti, *J. Electrochem. Soc., 127* (1980) 773.

70 C. W. Murphy, C. Cros, F. J. Disalvo and J. V. Waszczak, *Inorg. Chem., 16* (1977) 3027.

71 M. S. Whittingham, *Mater. Res. Bull., 13* (1978) 959.

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

73 B. Van Laar and D. J. W. Ijdo, *J. Solid State Chem., 3* (1971) 590.

74 G. L. Holleck and J. R. Driscoll, EIC Corporation, Newton, Ma., U.S.A., unpublished results.

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

76 F. A. Trumbore, *Pure Appl. Chem., 52* (1979) 119.

77 A. J. Jacobson, R. R. Chiannelli, S. M. Rich and M. S. Whittingham, *Mater. Res. Bull., 14* (1979) 1437.

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

79 A. H. Thompson and M. S Whittingham, *Mater. Res. Bull., 12* (1977) 741.

80 A. H. Thompson and M. S. Whittingham, *U.S. Patent 4,049,879* (1976).

81 A. LeMehaute, G. Ouvrard, R. Brec and J. Rouxel, *Mater. Res. Bull., 12* (1977) 1191.

82 A. LeMehaute and P. Perch, in J. Thompson (ed.), *Power Sources 7,* Academic Press, London, 1979, 623.

83 M. S. Whittingham, *U.S. Patent 4,049,887* (1976).

84 P. Palvadeau, J. Rouxel and M. Armand, *French Patent* (1976).

85 P. Palvadeau, L. Coic, J. Rouxel and J. Portier, *Mater. Res. Bull., 13* (1978) 221.

86 E. T. Mass, J. M. Longo and C. H. Chang, *U.S. Patent 4.093,783* (1978).

87 M. Armand, L. Coic, P. Palvadeau and J. Rouxel, *J. Power Sources, 3* (1978) 137.

88 R. Schollhorn, M. Kimpers and J. O. Besenhard, *Mater. Res. Bull., 12* (1977) 781.

89 M. Eisenberg, *U.S. Patent 4,136,233* (1979).

90 M. Eisenberg, *Proc. 28th Power Sources Symp.,* Atlantic City, N.J., June 1978, The Electrochem. Soc., Princeton, N. J., U.S.A., 1978.

91 M. Eisenberg, in B. B. Owens and N. Margalit (eds.), *Ambient Temperature Lithium Batteries,* The Electrochemical Society, Princeton, N.J., U.S.A., 1980, PV80-4.

92 A. J. Jacobson, M. S. Whittingham and S. M. Rich, *J. Electrochem. Soc., 126* (1979) 887.

93 A. J. Jacobson and L. E. McCandlish, *J. Solid State Chem., 29* (1979) 355.

94 J. P. Gabano, G. Lehmann, G. Gerbier and J. F. Laurent, in D. H. Collins (ed.), *Power Sources* 3, Oriel Press, Newcastle upon Tyne, England, 1971.
95 M. R. Kegelman, *U.S. Patent 3,847,674* (1974).
96 M. Eisenberg, *U.S. Patent 4,148,977* (1979).
97 M. Eisenberg and M. Willis, Fall Meeting of the Electrochem. Soc., Atlanta, GA, U.S.A., 1977, *Abstr. No. 11.*
98 J. O. Besenhard, *Z. Naturforsch., 33B* (1978) 279.
99 A. W. Murphy, F. J. DiSalvo, J. W. Carides and J. W. Waszczak, *Mater. Res. Bull., 13* (1978) 1395.
100 C. R. Walk and J. S. Gore, *J. Electrochem. Soc., 12* (1975) 68C.
101 D. W. Murphy, P. A. Christian, F. J. DiSalvo and J. W. Carides, *J. Electrochem. Soc., 126* (1979) 497.
102 K. M. Abraham, J. L. Goldman and G. L. Holleck, Fall Meeting of the Electrochem. Soc., Hollywood, Florida, 1980, *Abstr. no. 48.*
103 J. O. Besenhard and R. Schollhorn, *J. Electrochem. Soc., 124* (1977) 968.
104 L. Campanella and G. Pistoia, *J. Electrochem. Soc., 118* (1971) 1905.
105 H. F. Hunger and J. E. Ellison, *Rep. Eradcom, DELET-TR-78-23,* U.S. ERADCOM, Fort Monmouth, N. J., U.S.A., 1978.
106 M. Icovi, S. Panero, A. D'Agate, G. Pistoia and C. Temperoni, *J. Electroanal. Chem., 102* (1979) 343.
107 P. A. Christian, J. N. Carides, F. J. DiSalvo and J. V. Waszczak, *J. Electrochem. Soc., 127* (1980) 2315.
108 K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, *Mater Res. Bull., 15* (1980) 783.