RECENT DEVELOPMENTS IN SECONDARY LITHIUM BATTERY TECHNOLOGY

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Summary

Recent advances in ambient temperature secondary Li battery technology are discussed. An important recent development concerns the discovery of 2-methylfuran and related additives, enabling high efficiency Li cycling in tetrahydrofuran-based solutions. Five A h Li/TiS_2 cells utilizing the new electrolyte have exceeded 225 cycles at 60% depth-of-discharge, along with showing good discharge rate capabilities at -20 °C. Other systems currently being pursued include the Li/MoS_2 battery and SO_2-based cells. Some directions for future research and development are indicated in the light of present status and future needs.

Introduction

Ambient temperature rechargeable Li battery technology has become one of considerable diversification. Thus, systems based on both liquid and solid electrolytes are being pursued for a variety of civilian and military applications. All-solid-state Li batteries which incorporate Li^+-conducting solid electrolytes are expected to have wide ranging applications in the electronics industry. However, work in this area is still in the early stages of research, and few practical devices have thus far emerged.

Conventional ambient temperature secondary Li batteries have employed solutions of inorganic Li salts in organic solvents. We have recently reviewed developments in this technology to the end of 1981 [1]. A reason for its slow evolution in comparison with many primary Li batteries has been the difficulty in obtaining acceptable rechargeability for the Li electrode in organic media. Considerable progress has been made recently. A key turn of events was the recognition of the utility of aliphatic ethers as highly desirable electrolyte solvents for the electroplating and stripping of Li with high efficiency [1]. Consequently, organic electrolyte cells having capacities between 2 and 20 A h have been fabricated recently with a range of positive electrodes including TiS_2 [2], V_6O_{13} [3, 4], $Cr_{0.5}V_{0.5}S_2$ [5], MoS_3 [6] and MoS_2 [7].

More recently, attention has also turned to all-inorganic systems based on solutions in SO_2 [8, 9]. However, few details have so far been published.

Ether electrolyte batteries

Figure 1 depicts conductivities of a number of ethereal solutions. There are several interesting trends. In the same solvent, $LiClO_4$ solutions have lower conductivities than $LiAsF_6$ solutions. For the same salt, solutions in methylated cyclic ethers show lower conductivities than in their unmethylated analogs. Interestingly enough, the lower conducting 2-methyltetrahydrofuran (2Me-THF)/$LiAsF_6$ permits significantly higher efficiency Li cycling than does the higher conducting tetrahydrofuran (THF)/$LiAsF_6$ [10]. It has been proposed that reactions of the type in eqn. (1) are significantly slower with 2Me-THF [10, 11] and that this lowered reactivity is responsible for the superior Li cycling in 2Me-THF.
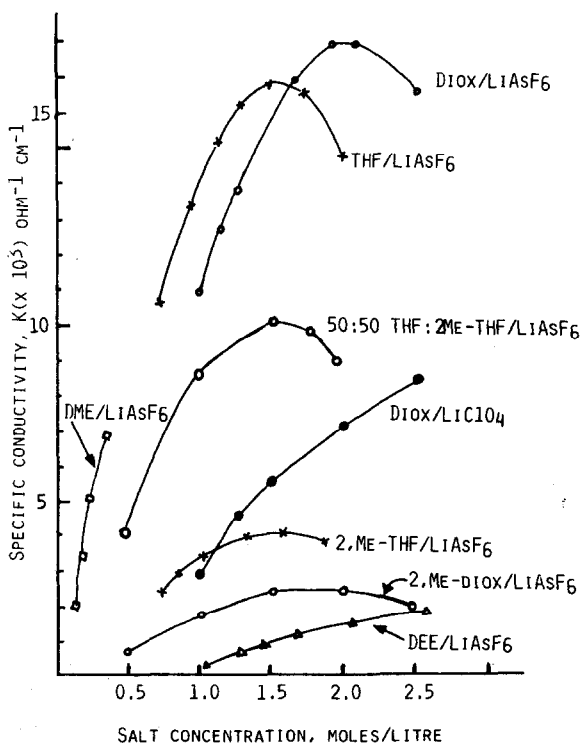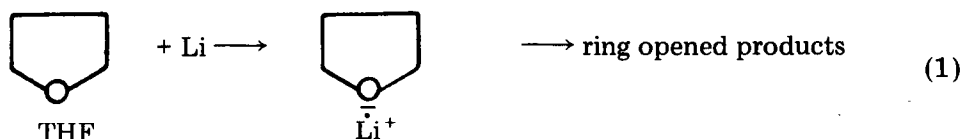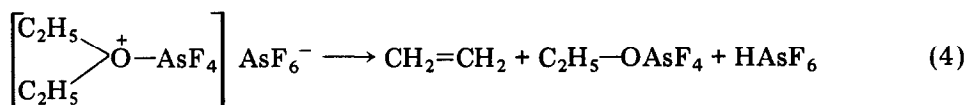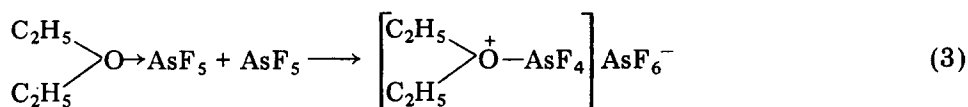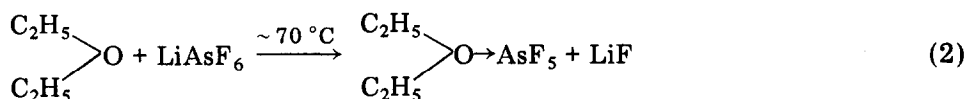

Fig. 1. Conductivities of ether electrolytes. Diox = 1,3-dioxolane; THF = tetrahydrofuran; DME = dimethoxyethane; DEE = diethylether.

$$\text{THF} + Li \longrightarrow Li^+ \longrightarrow \text{ring opened products} \tag{1}$$

Solvent reactivity sometimes involves interactions with the salt. An example is the diethyl ether (DEE) solution of $LiAsF_6$. Lithium cycles well in (DEE)/$LiAsF_6$ at very low Li charge densities [12]. This advantage vanishes, however, at the higher Li charge densities of 7 - 10 mA h/cm^2 [13]. Reactions between $LiAsF_6$ and DEE, shown in eqns. (2) - (4), are believed to be responsible for this poor efficiency Li cycling found in practical cells [13].
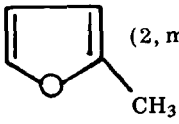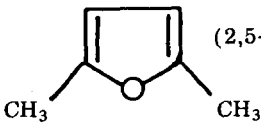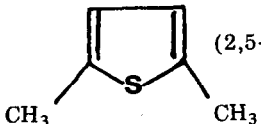
$$\underset{C_2H_5}{\overset{C_2H_5}{>}}O + LiAsF_6 \xrightarrow{\sim 70\,°C} \underset{C_2H_5}{\overset{C_2H_5}{>}}O{\rightarrow}AsF_5 + LiF \tag{2}$$

$$\underset{C_2H_5}{\overset{C_2H_5}{>}}O{\rightarrow}AsF_5 + AsF_5 \longrightarrow \left[\underset{C_2H_5}{\overset{C_2H_5}{>}}\overset{+}{O}-AsF_4\right]AsF_6^- \tag{3}$$

$$\left[\underset{C_2H_5}{\overset{C_2H_5}{>}}\overset{+}{O}-AsF_4\right]AsF_6^- \longrightarrow CH_2=CH_2 + C_2H_5-OAsF_4 + HAsF_6 \tag{4}$$
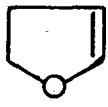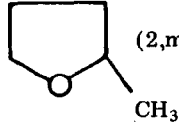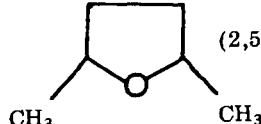
Except for its high reactivity with Li, the THF/$LiAsF_6$ solution is highly desirable for use in secondary Li batteries. It exhibits high conductivity at low temperatures (viz., below $-20\,°C$), and it is characterized by good thermal stability up to $70\,°C$ [14]. In an earlier paper [14] we reported that $LiAsF_6$ solutions in mixed solvents comprising THF and 2Me-THF enable relatively good Li cycling, despite substantial amounts of THF. We attributed this to Li-protecting films which form from reactions involving 2Me-THF. The films apparently help to retard the kinetics of the Li–THF reactions.

2-Methylfuran and related additives

Reinforcing the important role of Li surface films on high efficiency Li cycling in organic media is our most recent discovery [15, 16] of efficient Li cycling in THF solutions. We have achieved high efficiency Li cycling in THF/$LiAsF_6$ and in $LiAsF_6$ solutions in 2Me-THF/THF blends by the use of small amounts of unsaturated organic additives such as 2-methylfuran (2Me-F). In Table 1 we list several unsaturated cyclic ethers which have been found to effect varying extents of improvements of Li cycling in THF/$LiAsF_6$.

TABLE 1

Effect of additives on the cycle lifes of Li/TiS_2 laboratory cells utilizing $THF/LiAsF_6$ (1.5M)

Additive	Percent. by volume (vol.%)	Number of cycles*
None	—	7
(furan)	0.5	46
(2, methyl-furan) CH_3	0.5	110
CH_3 (2,5-dimethyl-furan) CH_3	0.5	37
CH_3 (2,5-dimethyl-thiophene) CH_3	0.5	38
(3,4-dihydrofuran)	0.5	28
(2,methyl-tetrahydrofuran) CH_3	0.5	10
CH_3 (2,5-dimethyl-tetrahydrofuran) CH_3	0.5	8

*Obtained at 1 mA/cm^2 with a capacity of 7 mA h/cm^2. Compare with Fig. 5 of ref. 13.

2-Methylfuran has been found to be the most effective additive to date. Laboratory Li/TiS$_2$ cells utilizing THF/LiAsF$_6$ plus 0.5 volume percent. (vol.%) 2Me-F exhibit about 100 cycles as opposed to 7 in 2Me-F-free cells. Our present data indicate the 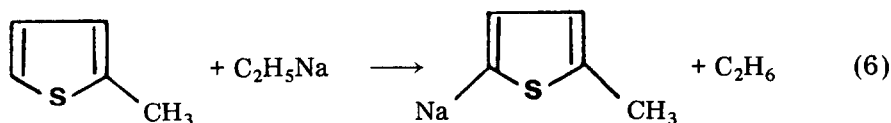requirement of at least one unsaturated center in the additive. We have also found that there is a stoichiometric relationship between the amount of effective 2Me-F and the Li being electrochemically cycled. Thus, about 0.4 mmole of 2Me-F is required per 1 A h of Li for the manifestation of an optimum additive effect. in THF/LiAsF$_6$ or its blends with 2Me-THF. This Li to additive mol ratio has been satisfactorily tested in 5 A h prismatic Li/TiS$_2$ cells (*vide infra*).

We believe that 2Me-F is effective as a cycle-life enhancing additive because it forms protective films on the Li surface. The film may be of the solid electrolyte [17] or of the polymer electrolyte type [18], enabling Li discharge and charge, while preventing, or significantly slowing down, direct chemical reactions at the Li surface. Our efforts to elucidate the nature of these surface films are in progress. Nevertheless, the metallation reactions of 2Me-F [19] and 2-methylthiophene [19] given in eqns. (5) and (6) are note-worthy, and the Li film composition could bear resemblance to these metallated products.

$$\text{(structure)} + C_2H_5Na \longrightarrow \text{(structure)} + C_2H_6 \qquad (5)$$

2,Me-Furan

$$\text{(structure)} + C_2H_5Na \longrightarrow \text{(structure)} + C_2H_6 \qquad (6)$$
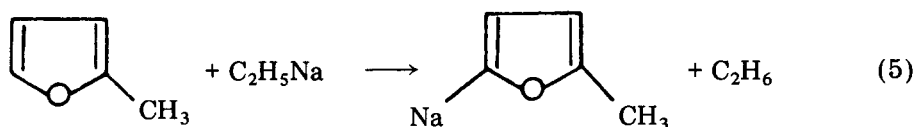
2,Me-Thiophene

We have also found that 2Me-F improves the cycle life of cells con-taining 2Me-THF/LiAsF$_6$ [16]. Distilled 2Me-THF contains about 0.2 - 0.4 vol.% of 2Me-F as an impurity [13]. Most of our earlier studies have utilized 2Me-THF solutions with this amount of 2Me-F. Recently, we have found that this 2Me-F can be completely converted to 2Me-THF by hydrogenating the "impure solvent" over a Pt catalyst at normal temperature and pressure [15]. Li/TiS$_2$ laboratory cells [13] using the 2Me-F-free-2Me-THF/LiAsF$_6$ solution have exhibited about half the number of cycles of cells utilizing the "regular electrolyte" with 0.2 - 0.4% 2Me-THF [16]. We have concluded [16] from these studies that while 2Me-THF/LiAsF$_6$, as previously claimed [12], is less reactive in secondary Li cells than THF/LiAsF$_6$, cycle-lifes in the former solution can be significantly improved with added 2Me-F.

5 A h cells utilizing THF

In optimizing 2Me-F containing THF solutions for use in practical cells, we have evaluated the rate-capacity behavior and cycle life of 5 A h Li/TiS$_2$ cells. Studies have been carried out with LiAsF$_6$ solutions in THF, 50:50 THF:2Me-THF, and 2Me-THF. These prismatic cells have been of the same type as we have previously described [2, 4].

Rate-capacity data obtained at 25 and −20 °C are given in Figs. 2 - 4. At room temperature, the observed trend in the rate capabilities of the cells follows solution conductivities. At −20 °C, however, the cell employing the mixed solution has yielded 50% of its capacity at 2 mA/cm^2, while capacities were non-existent at −20 °C in cells utilizing the parent solutions. The superior −20 °C performance of the mixed solution over THF/LiAsF$_6$, despite the higher conductivity of the latter, may be related to more desirable Li$^+$-solvates in the blend, permitting better Li$^+$ diffusivities and a consequently high rate-capability. The 2Me-THF system is impractical below 0 °C because of the formation of sparingly soluble Li$^+$-solvates [13]. It should be noted that a significant fraction of the conductivity of Li salt solutions in organic solvents is due to anionic transference [20]. In Li insertion cathode cells, however, discharge rates are primarily governed by the transport of Li$^+$ in solution and in the solid cathode [21], both being influenced by Li$^+$-complexation. Recently, Besenhard et al. found [22] that limiting currents in insertion cathode cells employing a number of organic solutions, despite the same conductivity, were higher in those solutions with higher Li$^+$ concentrations.
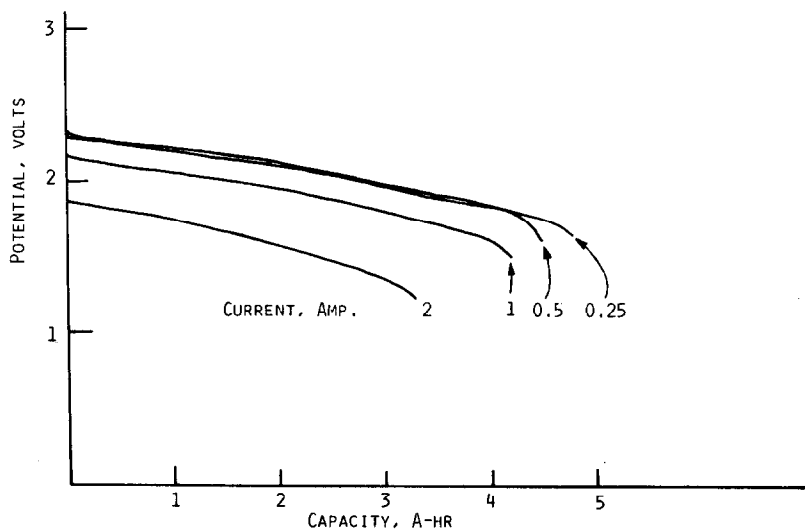

Fig. 2. Discharges at various currents at 25 °C in a 5 A h Li/TiS$_2$ cell utilizing the electrolyte, 48.3 vol.% THF:48.3 vol.% 2Me-THF:3.4 vol.% 2Me-F/1.5M LiAsF$_6$. Electrode area, 340 cm^2.
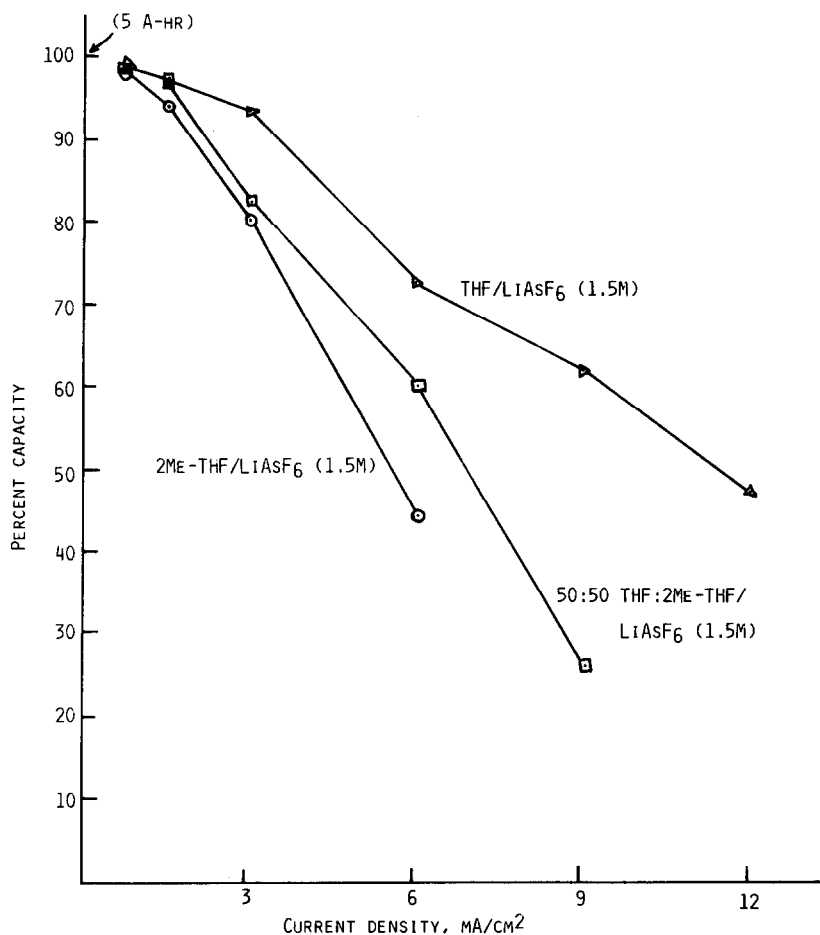
Fig. 3. Rate/capacity data obtained at 25 °C in 5 A h Li/TiS_2 cells with different electrolytes. For a given electrolyte, the whole data have been obtained using the same cell, with the recharge, following a discharge, being carried out at 0.5 mA/cm^2.

Cells utilizing the THF/2Me-THF blend plus 2Me-F solutions have also given the longest cycle life. Thus a 5 A h Li/TiS_2 cell with a solution of the composition, THF (48.3 vol.%):2Me-THF(48.3 vol.%):2Me-F(3.4 vol.%)/ $LiAsF_6$(1.5M), ran more than 225 cycles when cycled at a depth-of-discharge of 60%, Fig. 5. Under identical cycling regimes, 2Me-THF/$LiAsF_6$ cells (with 0.8 vol.% 2Me-F) have given 125 cycles, and THF/$LiAsF_6$ cells (with 3.4 vol.% 2Me-F) have given 120 cycles. In all cases cell failure occurred due to increased impedance and dendrite shorting.

The cycle-life presented in Fig. 5 appears to be the longest achieved to-date in a relatively high capacity practical cell. In our opinion, this is the first time that the capabilities of high rate discharges, at both room and low temperatures, and long cycle-lifes have become possible with the same solution.
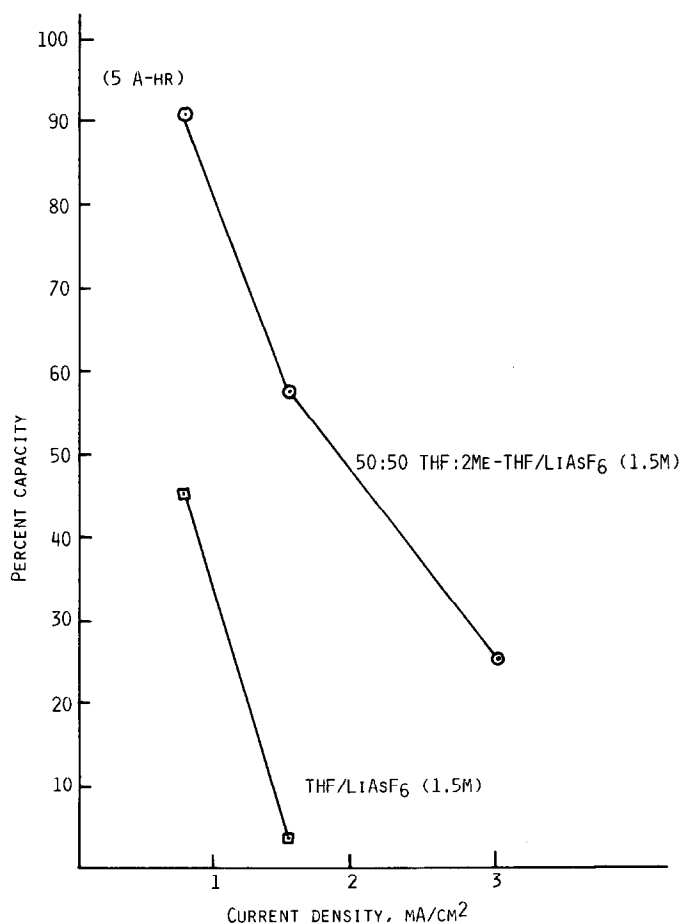
Fig. 4. Rate/capacity data obtained at -20 °C in 5 A h Li/TiS_2 cells.

Other areas of current interest

The Li/TiS_2 system, depending upon cell sizes, can deliver specific energies of 90 - 140 W h/kg and volumetric energy densities of 160 - 200 W h/litre. Clearly, highly rechargeable positive electrodes capable of specific energies and volumetric energy densities exceeding those of TiS_2 are desirable for many potential applications of secondary Li batteries. Various avenues are being explored.

Insertion cathodes

Numerous Li insertion cathodes with quasi-theoretical specific energy and energy densities higher than those of TiS_2 have been reported [1, 3, 23, 24]. Most of these materials, however, have not been investigated

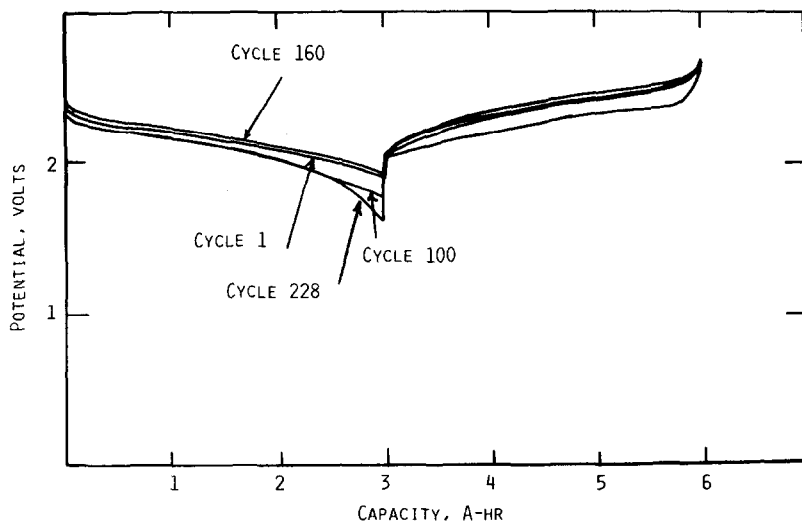Fig. 5. Typical galvanostatic cycles in a 5 A h Li/TiS$_2$ cell utilizing the electrolyte, 48.3 vol.% THF:48.3 vol.% 2Me-THF:3.4 vol.% 2Me-F/1.5M LiAsF$_6$. Current: cycles 1 and 100, i_d = 0.5 A, i_c = 0.25 A. Cycles 160 and 228, i_d = i_c = 0.25 A. Depth-of-discharge, 3 A h (60%).

beyond the laboratory cell level and their actual performance limits in practical batteries are not known.

Selecting a cathode material for a given application on the basis of laboratory cell data has inherent limitations. Practical cells in most instances are required to perform over a wide range of current density. Such performance capabilities should also be accessible during the entire cycle life of the cell. To achieve this level of performance it has been necessary in many cathode materials to use conductive and pore-forming additives such as carbon. Two such materials are V$_6$O$_{13}$ [4] and Cr$_{0.5}$V$_{0.5}$S$_2$ [5]. Because of substantial amounts of carbon, both of these cathodes have given significantly lower energy densities than those predicted by small laboratory cell data. Often, it is also difficult to obtain from short-term cycling in laboratory cells, information such as the effect of minor electrolyte–cathode chemical interactions on cell performance, and cathode shelf-life and self-discharge rates.

Amorphous transition metal chalcogenides and "metal-stable" Li insertion compounds comprise two classes of compounds which have received considerable recent interest as high energy density positives. Well known amorphous insertion electrodes include MoS$_3$ [25] and V$_2$S$_5$ [26]. In our hands [6, 27] a-MoS$_3$ was more reversible than a-V$_2$S$_5$. A serious problem with a-MoS$_3$ is its poor electronic conductivity. As a result of this, up to 30 wt.% carbon black was required in the cathode to obtain acceptable discharge rates and cycling performance. Our data from cells utilizing 2Me-THF/LiAsF$_6$ indicated that a useful area of research with a-MoS$_3$ would be

structural doping to improve its electronic conductivity. We have found [27] a-V_2S_5 to be poorly reversible, in agreement with the work of Jacobsen and Rich [26]. It appears from our data that a-V_2S_5 may be more appropriately represented as $VS_2 \cdot S_{0.5}$ in which the redox involving S becomes irreversible after the first few cycles. Amorphous materials must be carefully scrutinized to screen out structural irreversibilities such as that found in a-V_2S_5.

"Metal stable" insertion electrodes as a group have continued to receive research emphasis. Some examples are $Na_{0.1}CrS_2$ [28], $Li_xV_3O_8$ [29] and Li_xMoS_2 [30, 31]. None of the materials investigated to date seems to have energy density capabilities greater than that of TiS_2. These materials function as reversible cathodes because of a certain degree of initial Li insertion. Evidently the initial structural transformations brought about by the alkali metal insertion are the keys to their reversible performance.

The Li_xMoS_2 system is particularly interesting. Earlier, MoS_2 was abandoned as a low capacity, irreversible, insertion electrode [24]. Later studies [32] indicated that amorphous MoS_2 was superior to crystalline MoS_2. In the meantime, Haering *et al.* [30] found that if MoS_2 is allowed to discharge down to ~ 1 V in a Li cell, it inserts ~1 Li/mole with a concomitant structural transformation of the sulfide lattice. The Mo co-ordination changes from trigonal prismatic (TP) to octahedral (lT). This new lattice is preserved on subsequent cycling. Cell discharge/charge occurs between 2.2 and 1.3 V with a mid-discharge voltage of ~1.7 V. A C-size rechargeable Li_xMoS_2 cell has, apparently, been fabricated [7]. This cell has given 1.5 - 2 A h with a mean voltage of 1.7 V. It reportedly ran over 100 cycles.

Several oxide positive electrodes such as $LiCoO_2$ [33], Cr_3O_8 [34] and Mo-oxides [34] are potentially capable of providing cells with higher energy densities than the TiS_2 system. Because of their very high reduction potentials, however, the Co and Cr oxides cannot be used in combination with ether solutions. Solvents such as acetonitrile [1], propylene carbonate [1], and sulfolane [35], have high anodic stability, and the Co and Cr oxides may be used with them. Solutions in these solvents do not cycle Li well, however. In addition, sulfolane works well only above 50 °C [35]. Possible ways to make use of these high anodic range reactive solvents with the high voltage oxides are in combination with an alloy (*e.g.*, Li–Al [36] or an intercalation (*e.g.*, $LiWO_2$ [37]) negative electrode. The higher potentials of $LiCoO_2$ and Cr_3O_8 would compensate, at least in part, for the lower energy densities of these, presumably, more stable anodes.

A general drawback of many oxides is that they have a propensity for irreversible reduction upon extensive Li uptakes. Molybdenum [34] and V [4] oxides have shown this. Besenhard has suggested [34] that this may be due to the strongly negative free energy of formation of Li_2O ($\Delta G = -610$ kJ mol^{-1}), in comparison with Li_2S ($\Delta G = -465$ kJ mol^{-1}).

Recently, reports on several new oxide cathode materials have appeared [38, 39]. However, the full practical potential of these materials is not fully understood. Further scrutiny is certainly required before they qualify for practical applications.

SO$_2$ electrolyte batteries

    In the first version, SO$_2$ was used both as the cathode depolarizer and the electrolyte solvent [8]. Useful electrolytes include Li$_2$B$_{10}$Cl$_{10}$, LiAlCl$_4$ and LiGaCl$_4$. This cell apparently suffers from poor rechargeability because of mechanical degradations of the catalytic carbon electrode following deposition of the discharge product, Li$_2$S$_2$O$_4$.

    In the latest version, metal halides such as CuCl$_2$ and CoCl$_2$ are used as cathodes [9, 40] and SO$_2$ serves merely as the electrolyte solvent. Cathode reactions in the case of the CuCl$_2$ electrode seem to be those shown in eqn. (7).

$$\text{Li} + \text{CuCl}_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} \text{LiCl} + \text{CuCl} \tag{7}$$

The CuCl$_2$ cell has a flat discharge potential of ~ 3.4 V and a quasi-theoretical energy density of ~ 640 W h/kg. Very little information has been published regarding practical specific energy, volumetric energy density, discharge rate capabilities, low temperature performance, and cycle- and shelf-lifes.

    The seemingly good rechargeability of the metal halides in SO$_2$ is no doubt associated with their insolubility. Many metal halides or their discharge products are soluble in most organic solvents, making them impractical in such solvents [23]. The success with CuCl$_2$ suggests potential utility for many other metal halides as rechargeable cathodes in SO$_2$ or similar inorganic solvents.

Future prospects

    The future prospect for rechargeable Li cells appears to be very good. There are still major limitations to be overcome if the technology is to be used in broad-based applications.

    Some key items for future research and development are:
    ● Higher energy positive electrodes. They are needed to take advantage of the full potential of the Li technology. Studies of amorphous and metastable insertion electrodes would be fruitful in this respect. Polymer electrodes along the lines of (CH)$_x$ comprise another group of materials with potential for considerable versatility. Metal halides, oxides, sulfides, etc., in inorganic electrolytes offer potentially new opportunities.
    ● New and improved solutions to cycle Li with still higher efficiencies and to achieve better low temperature capabilities down to -40 °C. Understanding the structure and properties of mixed solvent electrolyte systems appears to be a key. Sulphur dioxide-based systems have opened up new possibilities for batteries based on all-inorganic components.
    ● Studies of the Li–electrolyte interphase; *i.e.*, investigations of the chemistry and physics of the films formed on the Li electrode in various electrolytes in order possibly to control and predict the kinetics of the Li–solution reactions and offer alternatives. The discovery of 2Me-F related additives is a key development on which to base further investigations.

•Development of improved separators to control dendrite shorting.

• A full elucidation of the safety features of the technology. A complete knowledge of the various chemical interactions is the key, and in this respect investigations modelled after the studies in primary cells [41, 42] would be useful.

Acknowledgement

References

1 K. M. Abraham and S. B. Brummer, in J. P. Gabano (ed.), *Lithium Batteries,* Academic Press, London, 1983, Ch. 14.
2 K. M. Abraham, J. L. Goldman, P. B. Harris, J. Avery and S. B. Brummer, *Abstract No. 314, Fall Meeting of the Electrochemical Society, Detroit, MI, 1982.*
3 D. W. Murphy and P. A. Christian, *Science, 205* (1979) 651.
4 K. M. Abraham, J. L. Goldman and M. D. Dempsey, *J. Electrochem. Soc., 128* (1981) 2493.
5 K. M. Abraham, P. B. Harris and D. L. Natwig, *J. Electrochem. Soc., 130* (1983) 2310.
6 G. L. Holleck, K. M. Abraham, P. B. Harris, J. L. Goldman, J. Avery, M. W. Rupich and S. B. Brummer, *Proc. 30th Power Sources Symp.,* Atlantic City, NJ, 1982.
7 J. A. Stiles, Lithium–molybdenum sulfide secondary cells, to be published in *Prog. Batteries Solar Cells.*
8 A. N. Dey and W. Bowden, *Duracell Final Rep. on Contract 4507410* to Lawrence Berkeley Laboratory, University of California, 1981.
9 W. L. Bowden and A. N. Dey, *Belgian Pat., BE895,143* (1983).
10 J. L. Goldman, R. M. Mank, J. H. Young and V. R. Koch, *J. Electrochem. Soc., 127* (1980) 1461.
11 V. R. Koch, *J. Electrochem. Soc., 126* (1979) 181.
12 V. R. Koch, J. L. Goldman, C. J. Mattos and M. Mulvaney, *J. Electrochem. Soc., 129* (1982) 1.
13 K. M. Abraham, J. L. Goldman and D. L. Natwig, *J. Electrochem. Soc., 129* (1982) 2404.
14 K. M. Abraham and J. L. Goldman, *J. Power Sources, 9* (1983) 239.
15 K. M. Abraham, S. B. Brummer and J. S. Foos, *U.S. Pat.* filed 1983.
16 K. M. Abraham, J. S. Foos and J. L. Goldman, *J. Electrochem. Soc., 131* (1984) 2197.
17 E. Peled, *J. Electrochem. Soc., 126* (1979) 2047.
18 M. Garreau and J. Thevenin, *Abstract No. 58, Fall Meeting of the Electrochemical Society, Washington, DC, 1983.*
19 H. Gilman and F. Breuer, *J. Am. Chem. Soc., 56* (1934) 1123.
20 G. E. Blomgren, in J. P. Gabano (ed.), in *Lithium Batteries,* Academic Press, London, 1983, Ch. 2.
21 S. Atlung, K. West and T. Jacobsen, *J. Electrochem. Soc., 126* (1979) 1311.
22 J. O. Besenhard, J. Heydecke, E. Wudy, H. P. Fritz and W. Foag, *Solid State Ionics, 8* (1983) 61.
23 K. M. Abraham, *J. Power Sources, 7* (1981/82) 1.
24 M. S. Whittingham, *Prog. Solid State Chem., 12* (1978) 41.

25 A. J. Jacobsen, R. R. Chiannelli, S. M. Rich and M. S. Whittingham, *Mater. Res. Bull.*, *14* (1979) 1437.
26 A. J. Jacobsen and S. M. Rich, *J. Electrochem. Soc.*, *127* (1980) 779.
27 K. M. Abraham, unpublished results with V_2S_5.
28 ·R. V. Moshtev, A. Nassalevska, G. Pistoia and M. Icovi, *J. Electrochem. Soc.*, *128* (1981) 1399.
29 S. Panero, M. Pasquali and G. Pistoia, *J. Electrochem. Soc.*, *130* (1983) 1225.
30 M. A. Py and R. R. Haering, *Can. J. Phys.*, *61* (1983) 76.
31 R. R. Haering, *U.S. Pat. 4,224,390* (1980).
32 A. J. Jacobsen, R. R. Chiannelli and M. S. Whittingham, *J. Electrochem. Soc.*, *126* (1979) 2277.
33 K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, *Mater. Res. Bull.*, *15* (1980) 783.
34 J. O. Besenhard, J. Heydeck and H. P. Fritz, *Solid State Ionics*, *6* (1982) 215.
35 S. P. S. Yen, B. Carter, D. Shen and R. Somoano, *Proc. 30th Power Sources Symp., Atlantic City, NJ, June, 1982.*
36 J. O. Besenhard, *Prog. Batteries Solar Cells*, *3* (1980) 87.
37 B. DiPietro, M. Patriarca and B. Scrosati, *J. Power Sources*, *8* (1982) 289.
38 R. J. Cava, D. W. Murphy and S. M. Zahurak, *J. Electrochem. Soc.*, *130* (1983) 2345.
39 M. Boccoli, F. Bonino, M. Lazzari and B. Rivolta, *Solid State Ionics*, *7* (1982) 65.
40 W. L. Bowden, *U.S. Pat. 4,409,303* (1983).
41 M. W. Rupich, L. Pitts and K. M. Abraham, *J. Electrochem. Soc.*, *129* (1982) 1857.
42 K. M. Abraham and R. M. Mank, *J. Electrochem. Soc.*, *127* (1980) 2091.