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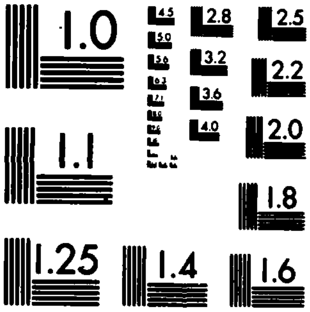

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AMBIENT TEMPERATURE RECHARGEABLE LITHIUM CELLS: STATE OF THE ART; PROBLEMS AND OPPORTUNITIES

by

S. B. Brummer

Prepared for Publication as a Chapter in the Book Lithium Battery Technology
Edited by H. V. Venkatasetty

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The state of the art in rechargeable lithium cells is reviewed. Striking advances were made in the 1970's. Systems based on Li/2Methyl tetrahydrofuran, $LiAsF_6/TiS_2$ are the most advanced. They show >200 cycles in small (<1 Ah) cells and ~100 cycles in larger (~5-20 Ah) cells. Limiting problems and future directions for research and development are discussed.

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AMBIENT TEMPERATURE RECHARGEABLE LITHIUM CELLS: STATE OF THE ART; PROBLEMS AND OPPORTUNITIES

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I. INTRODUCTION

There have been striking advances in rechargeable Li cells since 1974. In that year Selim and Bro (1) published a paper showing that Li deposits from PC*/$LiClO_4$ partially passivate, particularly on stand, and are not available for efficient discharge. They expressed the opinion that this results from an insulating film on the Li surface comprising solvent-metal reaction products. They regarded such reactions as inevitable in polar solvents, a consequence of the polarity itself, and were pessimistic about the practical possibilities for recharging Li. Experience since then has shown that Selim and Bro were correct about solutions in PC but that the situation is completely different in other solvents such as ethers.

As a result, it is now possible to build rechargeable Li cells which show over 100 deep cycles, as we shall report below. This is an emerging technology and promises to come into practical use in the late 1980's. Its major present niche of usefulness appears to be to substitute for Li primaries in medium rate (~ C/5), medium energy density (~50 *Wh/lb*) applications. A range of 50-200 cycles appears to confer large cost benefits.

Since we have recently reviewed advances in the field in very great detail (2) and there are several fairly recent reviews (3-7), we will here concentrate on very specific aspects of the field, those aspects which appear to be the most crucial for further progress.

In Section II, we briefly review the status of the rechargeable Li electrode, ca. October 1982. We will consider only organic solvent-based solutions. Ethers are the solvents of the moment and more progress can be expected in this direction. Our main emphasis here, however, is on the nature of the films on the Li surface in ethereal solvents and in pointing out the bottom line questions which need to be answered to advance the field. We also discuss the experimental methodology for measuring Li cycling efficiency, and we come as messengers bearing very bad news: We know of no rapid test for measuring Li cycling efficiency. As we show, shallow Li cycling, practiced by us and others in the laboratory, has no predictive value of performance in the "real world".

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*Solvent abbreviations are appended at the end of this chapter.

In Section III we deal with the rechargeable positive electrodes that can be used in Li cells. Again, because of the prior reviews (2,3,4), we will only deal here with the most promising materials. Titanium disulfide is the most highly developed of all those explored and works in our view best of all. However, its energy density is modest, 120 Wh/Kg in large, moderate rate batteries being the practical limit. It is our opinion that the energy density of practical systems must be improved (e.g., to 150-165 Wh/Kg at C/3 or >200 Wh/Kg at C/10), if this technology is to enjoy a large market penetration. Thus we explore possible options for improving the energy density.

Cycling and performance data for complete cells, with emphasis on recent, as-yet unpublished information, are surveyed in Section IV. We deal also in this section with cell safety and with a number of practical systems integration issues which must be solved.

In Section V we briefly summarize the key issues and suggest where more work is needed.

II. SOLVENTS AND SOLUTIONS FOR RECHARGING THE LITHIUM ELECTRODE

1. The problem in Recharging Li and Early Approaches to Solving It

The main issue has already been expounded above. Lithium can be plated from many solvents such as PC with virtually 100% efficiency (8,1) but it cannot be efficiently stripped. This is because as-plated Li reacts with the solution to form an insulating product film over part of its surface. This insulating film acts to isolate grannules of the metal from the substrate. The result is only moderate cycling efficiency and increasing passivation of the deposit on stand. As we discussed recently (2), this type of behavior completely eliminates PC from consideration as an electrolytic solvent in secondary Li cells.

There is a substantial difference between this type of phenomenology and that observed in ethers. In others, we also see less than perfect cycling efficiency and there is some loss of active Li mass on stand. These processes are largely reversible, however, and for example partially isolated deposits can be "recontacted" with freshly plated Li (6), an effect of major practical significance. As we shall see, there is indeed a controversy as to whether Li is filmed at all in some ethers.

We have reviewed in detail some of the approaches that have been taken to solve the reactivity-induced disturbance of Li plating morphology (2,5,6,7). The most important practical approaches have involved extremely careful purification, a topic we must emphasize because it is so important, and the choice of solvent. Here, we shall usually mention purification methods en passant and we shall dwell mainly on those results that most directly bear on the solvents found to be most useful for cycling Li, the aliphatic ethers.

2. Properties and Reactions of Electrolytic Solutions in Aliphatic Ethers

We have recently reviewed this area in considerable detail (2). Here, we briefly summarize the phenomena and then focus on the main questions concerning reactivity.

- 1,3-Dioxolane. Use of this solvent was pioneered by Garth (9) and subsequently by the group at Exxon (see (10) for a good summary). Diox/$LiClO_4$ is well conductive and cycles Li very well. It is, however, explosive (11).

Klemann and Newman (12) unambiguously assert that diox/$LiBR_4$ is stable towards Li, if the diox is carefully purified, e.g., by reduction with liquid Li/Hg amalgam at 95°C. Crucial in this purification is the removal of weak acid impurities in the diox which can form LiH on the surface of the Li. This LiH then goes on to react with more diox. They believe that this stability, and the stability of diox towards liquid Na-K, is without benefit of gross surface films on the metal.

Convinced of the stability of diox towards Li, the Exxon group looked hard for a suitable alternative to $LiClO_4$. They explored use of $LiAsF_6$ (12), which is highly conductive but which polymerizes the solvent (13), and $LiPF_6$ which does the same (10). There has been an extensive investigation of the Li alkyl/aryl borates (14,12,15,16,17) and, despite some sensitivity towards oxidation at the positive electrode (14,17), some promising leads have been uncovered (12). Our opinion is that more work is needed to confirm the practical usefulness of these solutes. The use of LiCNS was attempted and discarded (18) and the use of Li closoboranes was suggested (19). However, the latter involves addition of DME to the solution to assist solubilization of the salt and our experience is that DME is not stable towards Li in Li^+-containing solutions.

- Tetrahydrofuran and Its Derivatives. The group at EIC went in an opposite mode to the group at Exxon. We established the superiority of the solute $LiAsF_6$ for cycling Li in a whole range of solvents (20,21,22) and after that we mainly looked for an unreactive solvent for it. A major achievement of this search was the discovery of the usefulness of the solution 2Me-THF/$LiAsF_6$ for cycling Li (23,24). In our opinion this is the practical solution which cycles Li most efficiently.

We showed that THF reacts with Li and is apparently reduced (22,24, 25,26,27). The rate-limiting step appears to be addition of an electron to the hetero-atom. This is followed by relatively rapid decyclization. It is to be remarked upon that THF appears so easy to reduce whereas diox is apparently so very stable.

The electro-inductive effect of a 2Methyl group should slow down ring reduction and we certainly find that 2Me-THF/$LiAsF_6$ is a superior solution for cycling Li. However, we must be cautious about this line of reasoning because we so obviously see thick films on the metal surfaces in both THF and 2Me-THF solutions. Nevertheless, the data on the utility of 2Me-THF/$LiAsF_6$ solutions speak for themselves (23,24,27,28,29,30). The longest deep cycle life [260] we have reported was for a sealed Li/V_6O_{13} cell (29). We typically obtain 97.5% anode efficiency at 25 coul and 1 mA/cm^2 and 96.5% at 35 coul and 1.5 mA/cm^2.

For all their success in cycling Li, solutions of 2Me-THF/$LiAsF_6$ do have their problems. The conductivity is only moderate and rate performance of Li/TiS_2 cells is very poor below 0^oC, apparently due to solvate formation. This can be improved by addition of substantial amounts of THF, e.g., 50 vol % without catastrophic loss of cycling efficiency (30). This surprising result emphasizes once again the likelihood that 2Me-THF/$LiAsF_6$ is favorable for Li cycling because of the film it forms on the metal. In addition, we do see impedance buildup in cycled cells due to some reaction of the electrolyte and, as with THF, we see a brown film on the metal.

- Other Ethers. Koch et al. (31,32) reported spectacular results for solutions of $LiAsF_6$ in DEE with a variety of co-solvents. With 1 coul/cm^2 plates onto a Li substrate, a range of co-solvents showed cycle efficiencies of ~98.5%! Unfortunately, these solutions do not perform well in real cells and are thermally very unstable (33).

Foos et al. (34,35) found promising results for dimethoxymethane in shallow-plate half cells but only modest data (91.5 ± 0.5%) in 25 coul/cm^2 Li/TiS_2 cells. The solutions are well behaved thermally if purified inter alie by storing over Li (35) and show good low temperature performance.

The group at Exxon has frequently used DME as a co-solvent for diox (12,19). One value in this is that DME is an excellent bidentate coordinator of Li^+. In our opinion, DME is sensitized towards reduction by Li in presence of co-ordinating Li^+ ions.

- The Stability of Ethereal Solutions. Ethers are relatively easily oxidized (cf. ref. (17) and discussion in (2)). This is a problem with very oxidizing cathodes such as Cr_3O_8 or $LiCoO_2$ or polyactylene. Diox and THF (36) can be easily polymerized anodically.

There is no dispute that aliphatic saturated ethers readily react with bases (37,38) but there is some doubt whether they are reduced by alkali metals. Koch (22,24) presents evidence that THF is reduced by Li. Klemann and Newman (12) show that diox and many other ethers are not attacked by alkali metals, even liquid metals. This is a glaring discrepancy. The structural factors affecting the reactivity of ethers towards Li are urgently to be sought.

The thermal instability of ether/$LiAsF_6$ solutions can be a problem. 2Me-THF solutions are stable with Li at 71°C, even for 1 year (27,5). Solutions in THF are much less stable (27). At 100°C, no solutions could survive for more than a few hours (32). Those results are somewhat suspect, however, since we find thermal sensitivity in some systems (DMM, diox) in presence of air or after an alumina pretreatment (35). Solutions in DEE are particularly unstable (33).

3. Other Solvents Used for Lithium Cycling

Over the years there have been many (40). Two systems appear reasonably interesting at this time.

Carter et al. (41) and Somoano et al. (42) reported some interesting results for solutions in sulfolane and 3Me-sulfolane. The data are not quantitative, however.

Dey and Bowden (43) have reported on the usefulness of $Li_2B_{10}Cl_{10}$ in neat SO_2. Again no quantitative data are available.

4. Methodology for Testing Lithium Cycling Efficiency

Unfortunately the screening procedure we have used most frequently in recent years has turned out to have no predictive value whatsoever. Its one success was to discriminate the superior performance of 2Me-THF from 3Me-THF or pure THF. In this case, we find 96-97% for 1 coul/cm^2 Li-on-Li cycles in 2Me-THF and better than this in the real world. This is the only system in which we have found "real world" data to exceed half cell data.

The first sign of a serious problem arose with DEE. As we reported earlier (2), there are serious discrepancies between 1 coul/cm^2 (32) and 25 coul/cm^2 (33) plates in DEE-based solvents, as illustrated in Table 1. Of these systems, only 90 DEE-10 THF has an interesting cycling efficiency although this solution appears to have no obvious advantage over 2Me-THF/$LiAsF_6$. The data for the diox blend are most striking. They appear to suggest that diox reacts rapidly (with Li). This conclusion is premature, however. It may be that the diox is solvating a Li-DEE (polar) reaction product. This is analogous to the sensitization of DEE reactions with alkyl lithiums by addition of THF (38). Results in other systems are also illustrated in Table 1.

We see no correlation between the shallow Li-on-Li test cycling and the "real world". The real world, here, is essentially the test vehicle we have described earlier (28,29,45). We use realistic ratios of metal to solution and the system is held in compression. The time scale of a successful experiment is 90-150 days. In the half cell, the time scale is <24 hours, the ratio of solution volume to metal area is high and, most

TABLE 1

COMPARISON OF SHALLOW AND PRACTICAL Li CYCLES

Solvent	Shallow	Practical
DEE	97.9%	88.9%
90 DEE - 10 THF	98.0	96.3
90 DEE - 10 DME	97.9	92.0
90 DEE - 10 Diox	98.1	84.4
DMM	97 ± 0.5 (34)	90 ± 2
THF	88 (30)	58
2Me-THF	96-97	97.5 (29)

damning, there is great sensitivity of the results to experimental procedure, particularly to the addition of gases or treatments with absorbents (23-27).

We must then emphatically reject the predictions of our previously used Li-on-Li ~1 coul/cm^2 cycle test (27,32). Not only does this test not predict the outcome in real cells, it <u>does not even correlate with that outcome</u>. Notice, too, one other feature. The best looking deposits are in DEE. They appear specularly reflecting in thin layers (32). The best performance is with 2Me-THF/LiAsF$_6$. The deposit here is coarse and dendritic.

In passing, we wish to comment on a test we used in the early days of our Li cycling work and which seems to have cropped up again recently in the literature (41). This involves the use of a non-Li substrate with a thin Li plate. The advantage is that the cycling efficiency is obtainable (shallow) cycle-by-cycle, i.e., very quickly. The disadvantage is that the result is seems not to correlate with the real world. All the early work on Li cycling used thin plates on non-Li substrates (see (46) for a literature review). Many, as in ref. (41), have used an alloying substrate. We have several times reported on poor results due to solution reduction reactivity on the substrate when it is exposed each cycle (most recently in (20)).

What test can we do then that will mimic the real world but be quicker? To usefully guide a research program, we need a test that will show a "reliable" result in about a week. Here "reliable" implies at least a semi-quantitative correlation with the real world. We do not have a complete answer but we can suggest the criteria a test must meet. One important aspect of a test is to have a realistic metal surface to solution volume ratio. Also, the plate thickness must be greater than hitherto, at least in the range 5-10 coul/cm^2. To avoid loss of active material in the thick deposits that build up during the test, the plates must be held together in compression. To avoid dendritic shorting between the plates and to assure an appropriate area to volume ratio, the plates should each be bagged in a separator and spaced by a glass mat wick containing test solution. To avoid any problems with concentration polarization or dendrites, the current density must be kept down, e.g., to 1 mA/cm^2. Then, using a 1.5 mil Li foil substrate, a 90% efficient electrode would consume its substrate in ~100 h. A 95% efficient electrode would take ~200 h.

Preliminary data with this test (47) are promising and we will report on it in more detail later. It must be said that if this type of test does not work, we will have no choice but to guide our research with experiments in the real world.

5. The Role of Films on the Lithium Surface

We have already commented on the difference between the obvious films on the Li surface in solvents such as PC (or $SOCl_2$) and those in ethereal solvents (2,6). A notable difference is in the ability of the films to protect the metal from, for example, dissolved $AlCl^-_4$. In PC or $SOCl_2$, the $AlCl^-_4$ ion cannot reduce on the (insulating and non-porous) film and Li is plated under cathodic conditions. Al is plated from ethers.

Klemann and Newman (12) suggest that Li is stable against purified diox/$LiBR_4$ without benefit of films on its surface. However, surface films are very much a part of the AsF^-_6-ether-Li interface. We pointed out earlier that AsF^-_6 is reactive and takes a part in forming these films (6). We have noted brown films on the surface of cycled Li in THF or Me-THF (25,24). Both we at EIC (25) and the group at JPL (48) agree that this film contains As, F and O. It appears to result from reactions (reductions?) of both AsF^-_6 and the solvent.

In our view, the identity and the chemical and physical nature of these films are matters of very great urgency to advance the field. The effects of varying the anion and the solvent on film properties and on cycling efficiency must be sought. As long as this obvious area of reactive product accumulation remains largely unresolved, it is in our opinion premature to build elaborate theories relating solvent structure to reduction kinetics.

III. RECHARGEABLE POSITIVE ELECTRODES

1. General Survey

As patents often teach, there is a multiplicity of rechargeable positive electrodes that could be used in Li cells but (as they usually do not teach) most of these electrodes are not very useful in practice. In the light of earlier reviews (2-4), we will concern ourselves with the very useful or the very new.

Partially soluble (e.g., CuF_2) or completely soluble positives (e.g., Br_2 or Li_2S_{10}) have many possible advantages for high rate, low polarization and good chemical reversibility. The problem has been to control the self-discharge process and its rate (cf. (4) for review). Hence the more intensely scrutinized area recently has involved insoluble positives. It has become increasingly apparent that the small size of the Li^+ ion allows many structures to intercalate it with minimal lattice change. This phenomenon leads to high rate capability and excellent reversibility. Thus, a broad-based, world-wide search for low equivalent weight Li^+ ion intercalants has ensued. A favored class of compounds is the layered transition metal dichalcogenides.

Among all the layered dichalcogenides, TiS_2 has behaved by far the best in our hands. Therefore, we use it as the positive electrode in our present generation of rechargeable cells. It has the lowest equivalent weight of any single-Li^+-intercalating material in its chemical class. The chemistry of the Li_xTiS_2 phases is well behaved over the whole range of x (0 to 1); rate behavior and reversibility are excellent. Furthermore, Li_xTiS_2 is a good electronic conductor over its whole range of composition. Despite this, it is still necessary to use substantial amounts of carbon filler in practical porous electrodes. The purpose is to optimize porosity. We have recently reviewed our data in detail (2).

Among other layered dichalcogenides, the substituted VS_2's, e.g., $Cr_xV_{1-x}S_2$ ($0<x<1$) appeared to show some preliminary prospect of exceeding the energy density of TiS_2 (49,50). The main interest is that the cell voltage is higher as we add Cr (up to 2.6V for a mid-discharge potential vs. 2.1 for TiS_2). Recently, Abraham et al. (39,44,62) have shown that $Cr_{0.5}V_{0.5}S_2$ does cycle well but it requires a large amount of carbon for optimal performance. The overall effect is that $Cr_{0.5}V_{0.5}S_2$ is slightly worse than TiS_2.

One compound that has received considerable attention, particularly by the group at Bell Telephone Laboratories, is $NbSe_3$ (52,53). Up to $3e^-/NbSe_3$ can be obtained, although the potential is relatively low, ~1.8V). The material has three advantages: it is very reversible; it has good volumetric energy density, ~1 Wh/cm^3; it apparently needs no carbon filler (54). The last-mentioned is a substantial advantage: carbon may catalyze the reduction of some solutions, especially at the tail end of the discharge, and the carbon filler takes up a lot of space.

The amorphous sulfide MoS_3 showed initial results (55,2) which promised high energy density and long cycle life. However, a closer look (56) suggests that the solution reduces on the highly carbon filled (30%) MoS_3 electrode. This reduction process is especially rapid during overdischarge. Lithium/MoS_3 cells readily short due to Li dendrite formation on charge. These dendrites are especially severe because of the loss of electrolyte.

The reversibility of oxides in general (2) and V_6O_{13} in particular (29) is sensitive to overdischarge. This appears to be more severe with V_6O_{13} with a carbon filler, possibly implicating a role for solution reduction, as for MoS_3, but a factor nevertheless for all oxides. The Cr oxides (57) and $LiCoO_2$ (58) have interesting energy densities but their discharge potentials are too high for use with ethers.

Although outside the scope of this review, we will mention that the neat $SO_2/Li_2B_{10}Cl_{10}$ system is claimed to be reversible (43). We reviewed the available data on it earlier (2).

One possible class of positive electrodes, based on conductive polymers such as polyacetylene, has recently received much publicity (59,60). One reason for this attention is the hoped-for low cost of polymeric film electrodes. Another is the flexibility of battery design possible with such films. Further hopes are an easy property control via structural modifications of the polymer and low equivalent weight. So far, the data on the degree of reversible doping achieved in the anodic reaction

$$\left(CH \right)_x + yLiClO_4 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} \left[CH^{+y} (ClO_4)^-_y \right]_x + yLi$$

are very discouraging (59,60,61). Furthermore, this type of reaction occurs at very high potentials, too high for use of ethers, and the charged state involves a (heavy) anion. The latter degrades the possible energy density very severely.

2. How Can We Obtain Higher Energy Density?

In our view this is the crucial question. Lithium/TiS_2 cells can deliver up to 120 Wh/Kg in large modules at low rates. However, rechargeable Li cells will find their largest use applications not so much by increasing their life (100 cycles is good enough for most purposes and is in any case $\simeq$300 Ni-Cd cycles) as by increasing their energy density. We would suggest 200 Wh/Kg at low (< C/10) rates as a preliminary goal. The importance of improving the energy density arises because the natural advantage of Li cells is where performance is at a premium, e.g., in military applications, and the competition is often a Li primary cell.

One possibility, with the least need to change the other components of the system that work (i.e., the solution), is to explore further the amorphous sulfides (2,4). These have the potential in principle to improve the energy density of TiS_2 (equivalent weight 112, but at $0.7e^-/Ti$ the e.w is $\sim$160) by 50^+% ($3e^-/MoS_3$ corresponds to an e.w of 64).

A second possibility, also not requiring us to change the solution, is to use n-doped polymers as the positive electrode. An example is the reaction.

$$\left(CH \right)_x + nxLi \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \left(CH^{-n} \cdot Li_n^+ \right)_x$$

Here, the potential for the reduction of the polymer to its anion is invariably lower than for its oxidation to a cation. An ideal value would be $\sim$2.5V. This would allow use of ethereal solvents. Use of a Li^+ counter ion minimizes the equivalent weight of the positive electrode.

A third prospect is to use a very energetic positive ($LiCoO_2$ or Cr_3O_8 or polyacetylene with a light anion) in an oxidation resistant (to 5V vs. Li) solvent. Sulfolane may be a candidate for this purpose. Naturally, it is also necessary that the solvent resist attack by Li.

IV. RESULTS WITH COMPLETE CELLS

Results to date are somewhat limited but increasingly promising, more so than suggested in our most recent review (2).

The only cell made commercially, by Exxon, did not have a pure Li anode and was rated for only 5, 100% deep discharges. It was withdrawn from the market in 1979 when Exxon abandoned the solar-watch-Li-battery-powered business.

At EIC we have built and tested many ~0.6 Ah test cells (28,45). The earliest of these usually failed due to dendrite penetration of the separator (63) but this no longer a problem. We use this configuration routinely to evaluate solutions for Li cycling efficiency and positive electrodes. Cells are usually designed to show a life in the range 100-200 cycles with Li plates of 7-10 mAh/cm^2. Most of the EIC-originated data on cycling efficiency or cell performance are based on tests in this configuration.

We have also built a number of prototype prismatic Li/TiS_2 cells for evaluation of the technology under bona fide practical conditions. The very first group was supplied to JPL in 1979. They had dimensions of 5.5 x 5.7 x 1.8 cm and nominal capacities of 5 Ah at 300 mA. The cells were not tested for ~2 years. Two of them ran for ~50 complete cycles. Their life was limited by dendrites. A similar cell using a non-stoichiometric V_6O_{13} positive ran over 40 complete cycles before failing due to dendritic shorting (29).

To complete our survey of results with the first generation of cells, we must update the previous preliminary report on Li/MoS_3 cells with $LiAsF_6$ in 2Me-THF (2). Five ~20 Ah nominal cells were built and tested and showed quite disappointing results. All cells with two separator layers failed fairly quickly due to dendrite shorting. Post-test examination of the cells and analysis of their electrolytes showed that a main cause of failure was reaction of the electrolyte (56). All the cells showed high post-cycling electrolyte resistance and relatively little dissolved $LiAsF_6$. Unexpectedly, the solution reacted substantially at the positive. In particular the electrolyte reacted rapidly whenever the cell was overdischarged. There was loss of S from the MoS_3 and a gain of 30-50% in weight. Analysis showed some Li and F, H and O and a little As. A cell with 3 separator layers cycled over 50 times before shorting. In all cases, the capacity diminished substantially before final failure and the electrolyte resistance increased sharply (56).

Such results are not typical of Li/TiS_2 cells, although there is always some increase in cell impedance during cycling (62). It appears that the MoS_3 plus carbon positives (30% Shawinigan 50% compressed) are good catalysts for the reduction of the electrolyte. This may arise in part from the relatively low potential of the tail of MoS_3 reduction. Thus some electrolyte is reduced towards the end of every discharge. This effect is manifest when the cells are overdischarged. The rather great sensitivity of these cells to dendritic shorting is one result of this reactivity of the electrolyte. However, such reactivity of the electrolyte, although always observed, is not usually anything like so extreme. Abraham et al. (62,39,44) have recently reported on the cycling behavior of an 11 Ah nominal Li/$Cr_{0.5}V_{0.5}S_2$ cell and on the behavior of third generation Li/TiS_2 prismatic cells of the type discussed above. Results for these cells will be presented in detail elsewhere. We briefly survey them here.

The $Cr_{0.5}V_{0.5}S_2$ positive needs 20 wt % C, as against only 8% C with TiS_2, probably because of its moderately low conductivity. Typical discharge curves at 1A over 100 cycles are shown in Figure 1. The initial capacity is close to theoretical (10.9 Ah). There is an initial rapid loss of capacity down to ~9.9 Ah over about 5 cycles. Thereafter the capacity degrades relatively slowly until close to the end of life. At 100 cycles the capacity is still in excess of 8 Ah. The capacity-cycle number relation is shown in Figure 2. A cause of capacity loss is increase in impedance but even after 130^+ cycles, a capacity of ~90% of theoretical was obtained at low current densities.

Data for a third generation of Li/TiS_2 cells were also reported (62,51). This group of cells was intended as a test matrix and correspondingly they comprised a mix of constituents and constructions. Two-separator cells tended to short at ~50 cycles. The few three separator cells tested did not fail due to dendrite shorting but eventually due to impedance build-up. Their initial rate-capacity performance was good, as shown in Figure 3. They show close to 65% of theoretical at 1A.

Cycling performance is shown in Figure 4. The two cells cycled below 100% depth were discharged to 3 Ah on each cycle and fully recharged. The extent of the dotted lines shows the limit of a cell capacity of 3 Ah (respectively 54 and 60% of theoretical). These limits were reached in the range 80-90 cycles. Beyond this point, the full capacity was obtained on each cycle. It appears to decline more rapidly than suggested by the dotted line and this is in agreement with data for the 100% DoD cell (Fig. 4). In all cases there was resistive build-up during cycling but the electrolyte utilization was acceptable for practical utilization of the system, >14 Ah/ml. It is evident that the life-limiting factor in these cells is resistive build-up. A new generation of cells has been designed recently to mitigate this problem and to allow attainment of at least 3 Ah for at

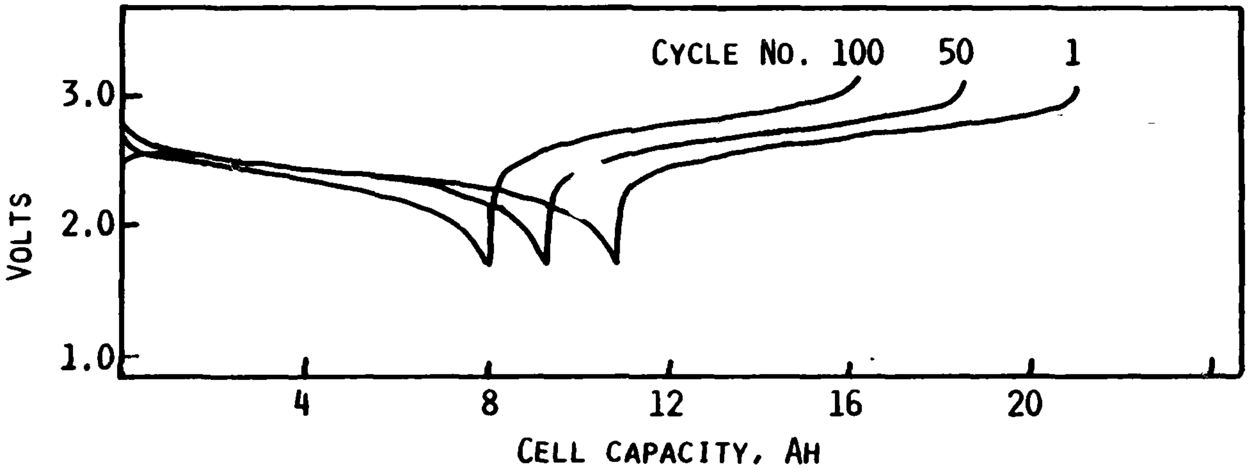

Fig. 1. Typical cycles of 11 Ah $Cr_{0.5}V_{0.5}S_2$ cell. Current: 1A, Voltage limits: 1.6-3.1V.

(Data from Abraham et al. (62) (39)).

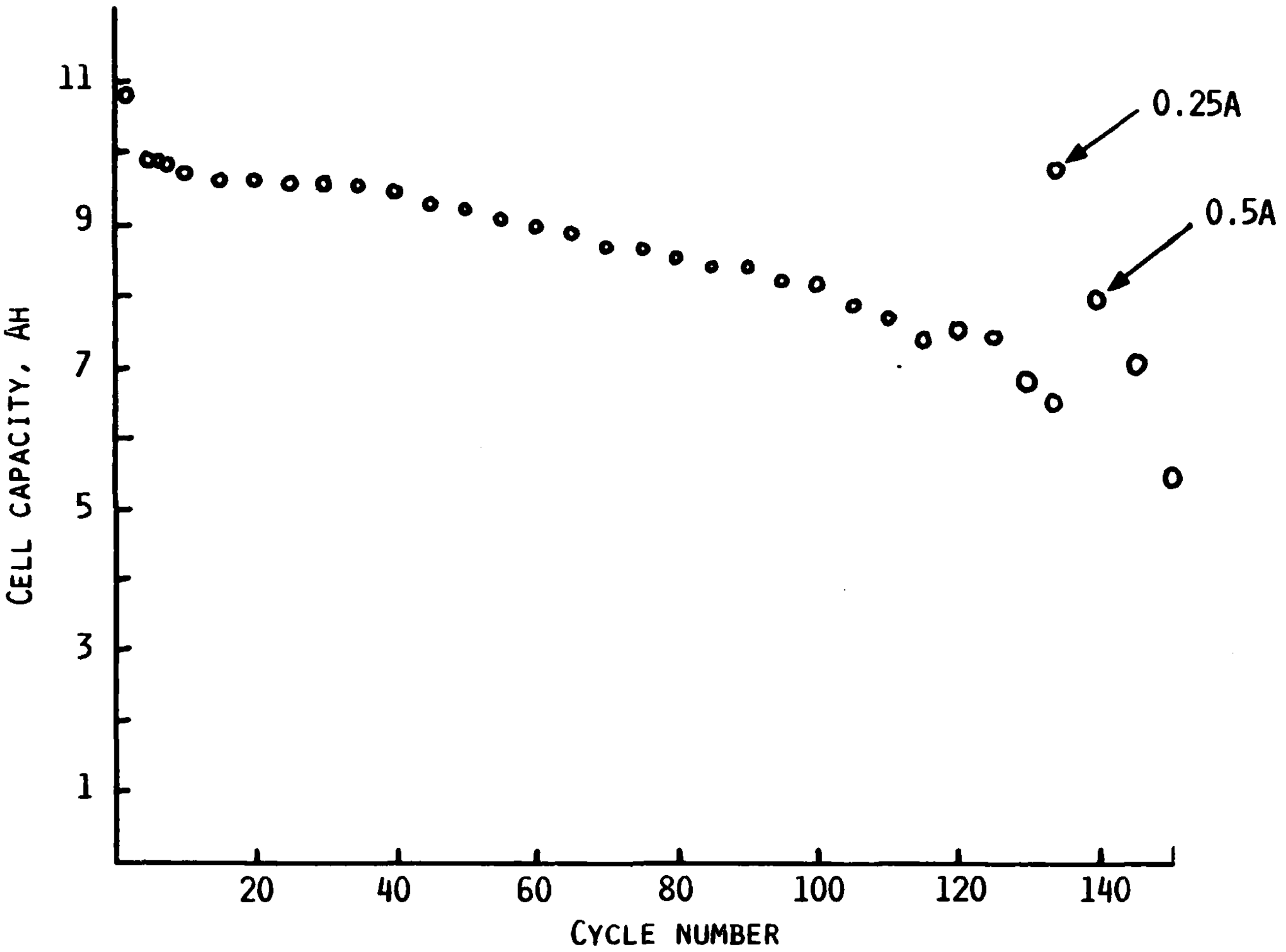

Fig. 2. Capacity versus cycle number in 11 Ah $Cr_{0.5}V_{0.5}S_2$ cell. Current: 1A; voltage limits: 1.6-3.1V.

(Data from Abraham et al. (62) (39)).

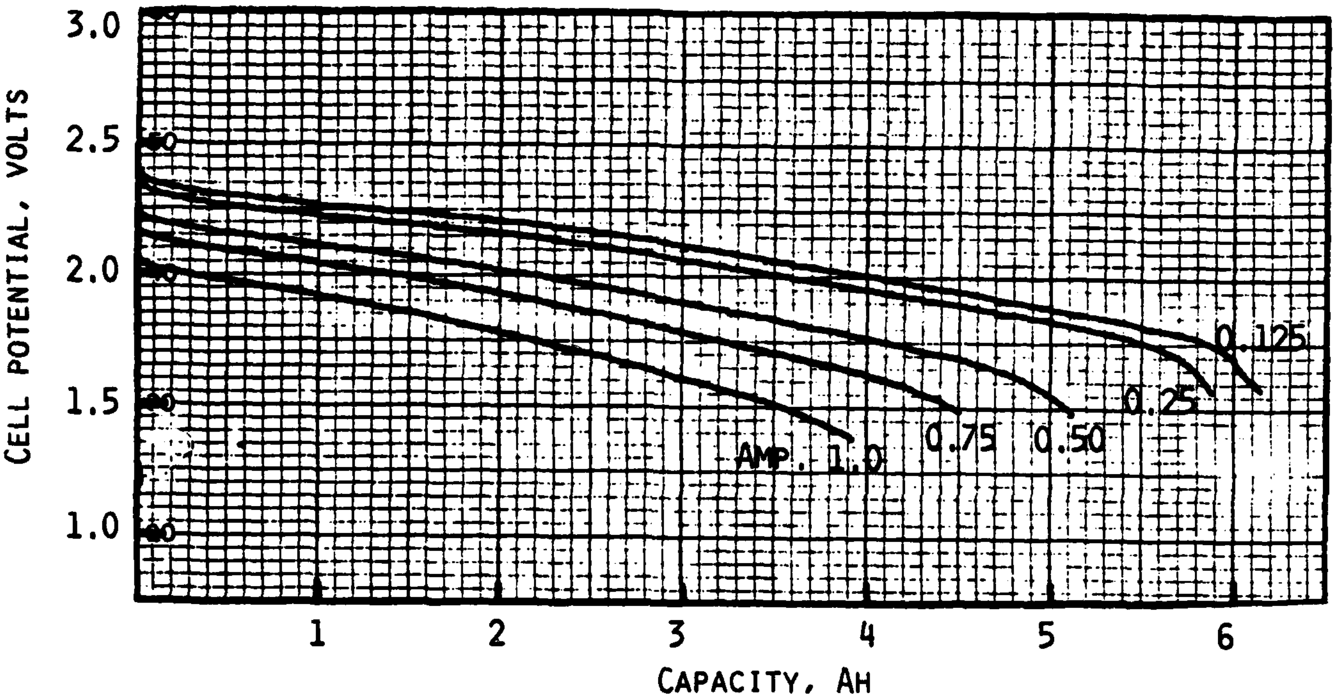

Fig. 3. Capacity versus current density for a 6 Ah Li/TiS$_2$ cell.

(Data from Abraham et al. (62) (51)).

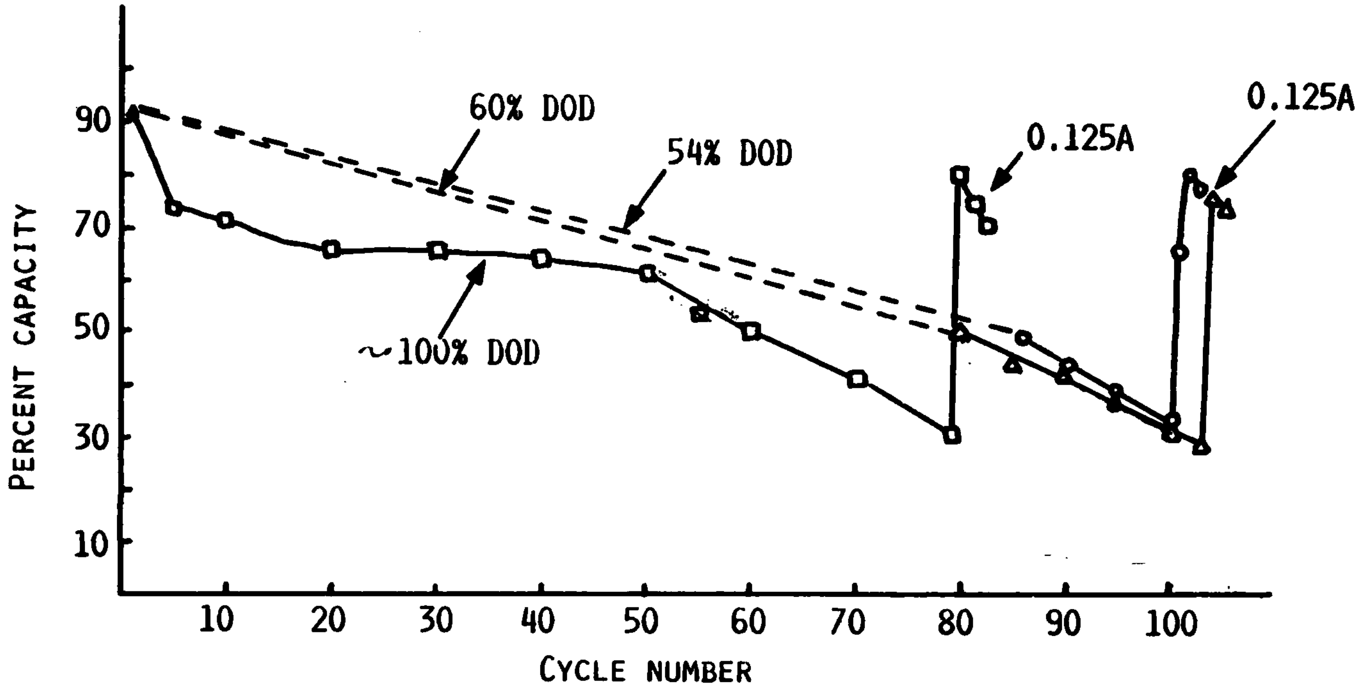

Fig. 4. Capacity versus cycle number in Li/TiS_2 prismatic cells. (Capacity 5-6 Ah: Current: 0.3A; voltage limits: 1.6-3.0V).

(Data from Abraham et al. (62) (51)).

least 100 cycles. It is evident that even now it is possible to obtain at least 4 Ah for at least 50 cycles.

The present design is not optimized. It occupies about 64 ml including the projection of the terminals and weighs ~120 g. Of these, we estimate that ~10% of the volume and 25% of the weight could be eliminated rather easily. Furthermore, it is to be noted that in this small size the can takes about 50% of the total weight. Based on projections of results from present cells, we would estimate the limits shown in Table 2 for the Li/TiS_2 cell. Small (<5 Ah) cells are not likely to exceed 100 Wh/Kg at medium to high rates or with high cycle life. Larger cells will probably exceed 120 Wh/Kg at medium to low rates.

In our hands, TiS_2 has exceeded the performance of all other positives in complete rechargeable cells. We believe, as stated above, that the technology still needs a more energetic positive if it is to achieve its market-place potential.

Two further system issues need attention also: More research on dendrite-resistant separators is required if the technology is to be applied with confidence to large cells. An overcharge mechanism will probably be required to facilitate battery charging and cell equalization. With larger batteries, cell-by-cell electronic control may be a useful alternative.

We have discussed safety recently (2), and it is premature to elaborate further on this topic here. We are fairly sure that rechargeable Li systems are safer than the most energetic primaries. One area where we have some concern is disposal. At the end of life, cycled Li cells have a high surface area negative electrode comprising a reactive mixture of Li interspersed with solution reaction products. When dry, this mixture appears to be shock/heat sensitive.

V. SUMMARY AND CONCLUSIONS

There have been striking advances in the state-of-the-art in recharging Li cells in the 1970's. Major discoveries were the utility of the ethereal solvents diox and 2Me-THF and the development of intercalation cathodes such as TiS_2. Cells based on Li/TiS_2 can now confidently be used 50-100 times and further extension of their life, to the range of ~200 cycles, appears highly probable. There are still major problems to be solved if the technology is to become used in broad applications:

- Extension of the useful range of the electrolyte to -40°C, whilst maintaining adequate cycle life. This is essential for many military applications.

TABLE 2

PROJECTIONS OF PERFORMANCE FOR Li/TiS_2 SYSTEM BASED ON ~3 CU IN. PRISMATIC CELLS

	Wh/Kg	Wh/Kg w/o Can
Over 50 cycles	93 each cycle	175
Over 100 cycles	70 each cycle	132
First few cycles at C/20	134 each cycle	252
First few cycles at C/4	82 each cycle	154

- Improvement of the energy density. This requires a more energetic positive electrode than TiS_2.

- Development of improved separators. This will be facilitated if we can improve solution conductivity.

- Internal cell overcharge mechanisms are essential to facilitate battery charging.

- A full elucidation of the safety features of the technology.

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SOLVENT ABBREVIATIONS

Diox	-	1,3-dioxolane
DEE	-	Diethylether
DME	-	Dimethoxyethane
DMM	-	Dimethoxymethane
2Me-THF	-	2Methyl Tetrahydrofuran
PC	-	Propylene carbonate
THF	-	Tetrahydrofuran

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