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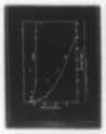






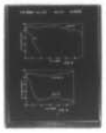








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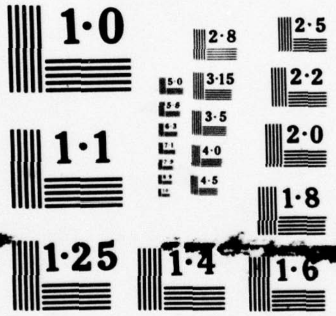

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MICROCOPY RESOLUTION TEST CHART

BASIC STUDIES OF THE LITHIUM SECONDARY ELECTRODE

TECHNICAL REPORT
for Period 01 February 1978 - 31 January 1979

CONTRACT NO. N0001-77-C-0155
TASK NO. NR 359-638

by

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April, 1979

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Arlington, Virginia 22217

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Rechargeable high energy density Li batteries require an efficient Li electrode. Earlier work with propylene carbonate (PC), methyl acetate (MA), and tetrahydrofuran (THF)-based electrolytes yielded poor Li electrode cycling efficiencies due to the electrolyte reduction by Li. We find 2-methyltetrahydrofuran (2-Me-THF)/$LiAsF_6$ media to be remarkably stable toward Li resulting in cycling efficiencies which approach 98%.

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20. Abstract (Cont.)

The ability of 2-Me-THF in particular, and $\underline{\alpha}$-methylated THFs in general, to resist reduction by Li is thought to be based on the position of its lowest unfilled molecular orbital (LUMO) relative to that of THF.

TABLE OF CONTENTS

I. INTRODUCTION

Tetrahydrofurans methylated in the α-position manifest remarkable chemical and electrochemical stability towards Li. While tetrahydrofuran (THF) distilled off benzophenone ketyl and stored with Li at 71°C reacts in two days, 2-methyltetrahydrofuran (2-Me-THF) treated similarly was stable for over 10 months. Electrolytes comprising either 2-Me-THF or 2,5-dimethyltetrahydrofuran (2,5-di-Me-THF) were subjected to cycling studies in half-cell configurations. Average Li on Li cycling efficiencies approached 98% for $Q = 1$ coul/cm^2. Freshly deposited Li from 2-Me-THF electrolyte subsequently stored on open circuit afforded an average isolation rate of 1.1 μA/cm^2 (96 hr). By comparison, Li plated from a THF electrolyte completely reacted in 48 hr, and after only 24 hr, the calculated isolation rate was 8.3 μA/cm^2.

Unlike the α-methylated ethers, 3-methyltetrahydrofuran (3-Me-THF) was as reactive towards Li as THF. Thus, the position of the methyl substituent with respect to the cyclic ether's oxygen atom is critically important. These results suggest that α-methyl substituents raise the lowest unfilled molecular orbital (LUMO) of the cyclic ether, which in turn retards its rate of reduction by Li.

II. 2-METHYLTETRAHYDROFURAN/LITHIUM HEXAFLUOROARSENATE: A SUPERIOR ELECTROLYTE FOR THE SECONDARY LITHIUM ELECTRODE

The development of an ambient temperature secondary battery employing a Li negative has been actively pursued over the past 20 years (1). The key technical problem precluding the implementation of such batteries is the cycling behavior of the Li electrode. Metallic Li can be plated from organic media containing Li^+ ions onto a conducting substrate with 100% efficiency (2). However, anodic dissolution of the reactant is invariably less than 100% efficient (2-4). The difference reflects residual Li metal electrically isolated from the conducting substrate by insulating films (1,5). These films arise from the reaction of freshly deposited Li with the electrolyte and protect the metal from further attack. The presence of such filmed or "encapsulated" Li particles results in an irregular surface which seriously distorts the subsequent morphology of the reactant. On the second cycle, for example, Li nucleation and growth proceeds irregularly; the surface area of the Li increases; the rate of reaction with electrolyte increases; and more Li is isolated. Thus, the effect of a small morphological perturbation on the first cycle becomes compounded over several cycles, leading to ultimate electrode failure.

A well-behaved Li electrode is contingent upon the development of a medium kinetically, if not thermodynamically, inert towards Li. Our work has involved the study of a variety of aprotic organic solvent and supporting electrolyte combinations, and the best results to date have been achieved with cyclic ethers in general and 2-methyltetrahydrofuran (2-Me-THF) in particular (6). In this paper, we compare solutions of $LiAsF_6$ in THF and 2-Me-THF in terms of their physical properties and relative inertness towards Li.

At 25°C, the density and viscosity values for 2-Me-THF correspond closely to those of THF: 0.880 g/cc, 0.461 cp (7), and 0.848 g/cc, 0.457 cp (8), respectively. However, the addition of a methyl group <u>α</u> to THF's oxygen atom seriously affects solution conductivity. The specific conductance at 25°C of 1M $LiAsF_6$/cyclic ether was found to be 3.0×10^{-3} $ohm^{-1}\ cm^{-1}$ for 2-Me-THF, and 13.7×10^{-3} $ohm^{-1}\ cm^{-1}$ for THF. The almost fivefold reduction in conductivity on going from THF to 2-Me-THF electrolyte may be ascribed to increased ion pairing in the latter (7,8). Possibly, the steric bulk of the 2-methyl group inhibits coordination between Li^+ and the nonbonding orbitals on the oxygen atom of 2-Me-THF. Thus, Li^+ is not solvated as completely by 2-Me-THF as it is by THF. We may note that the conductivities (1M $LiAsF_6$, 25°C) of electrolytes made with 3-Me-THF and 2,5-di-Me-THF straddle that for 2-Me-THF (i.e., 7.4 x 10^{-3} and 0.2 x 10^{-3} ohm^{-1} cm^{-1}, respectively), which is consistent with this model. Accordingly, the use of electrolytes comprising alkylated THFs may be restricted to low rate (<10 mA/cm^2) battery applications. While high conductivity is an important consideration in choosing an electrolyte, the fundamental criterion in the selection process is stability towards Li and, in this regard, 2-Me-THF is a notable step forward.

The stability of these cyclic ethers towards Li was assessed under static and dynamic conditions. Static tests involved the incubation of Li foil with electrolyte at 71°C. The onset of Li-electrolyte reaction visually manifests itself in terms of corrosion products on the Li foil and concurrent yellowing of the electrolyte. Dynamic conditions were achieved by cycling Li to and from Li or Ni substrates at 25°C. In this case, a fresh Li surface comes into contact with electrolyte on every cycle. Li-electrolyte reactivity was noted in terms of a loss of cycling efficiency with increasing cycle number.

Static tests revealed that 2-Me-THF distilled off benzophenone ketyl ($\phi_2CO^{-\cdot}$, Na^+) and sealed in Pyrex manifested no visible sign of reaction over a 10-month storage period. Contradistinctively, THF similarly treated reacted with Li in just 3 days; and, while solutions of $LiAsF_6$ and 2-Me-THF were stable over a 13-month period, $LiAsF_6$/THF media reacted after 25 days. Presumably, impurities introduced by the $LiAsF_6$ form protective films (9), or the salt itself can scavenge reactive intermediates. The major reduction product in the reaction of THF with Li was found to be n-butanol from lithium n-butoxide after hydrolysis (10).

A more stringent test of electrolyte inertness involves the dynamic cycling of Li to and from a conducting substrate. This mimics the charge and discharge characteristics of the Li electrode in a secondary cell. As mentioned earlier, good cycling efficiency (defined as charge stripped/charge plated) can only be achieved if the electrolyte is kinetically stable to Li. This requires an absence of reactive impurities as well as the chemical compatibility of salt and solvent towards Li. In Figure 1, the cycling efficiencies of THF and 2-Me-THF electrolytes on Ni are presented as a function of cycle number for 1.1 $coul/cm^2$ Li plates. (Although 50-100 $coul/cm^2$ of Li would nominally be cycled in a practical cell, thin plates are useful in rapidly assessing the quality of a given electrolyte. Cycling of thin plates many times exacerbates conditions leading to inefficiencies and electrode failure.) On the 10th cycle run in THF-based electrolyte, 80% of the Li plated is encapsulated by films and lost to anodic dissolution. By comparison, only 7% of Li plated from 2-Me-THF based electrolyte is electrically isolated. This electrolyte nevertheless does degrade with cycling number, as evidenced by the decay of cycling efficiency. Either reactive impurities and/or a very slow reaction of 2-Me-THF with Li yield products which perturb the morphology of subsequent plates.

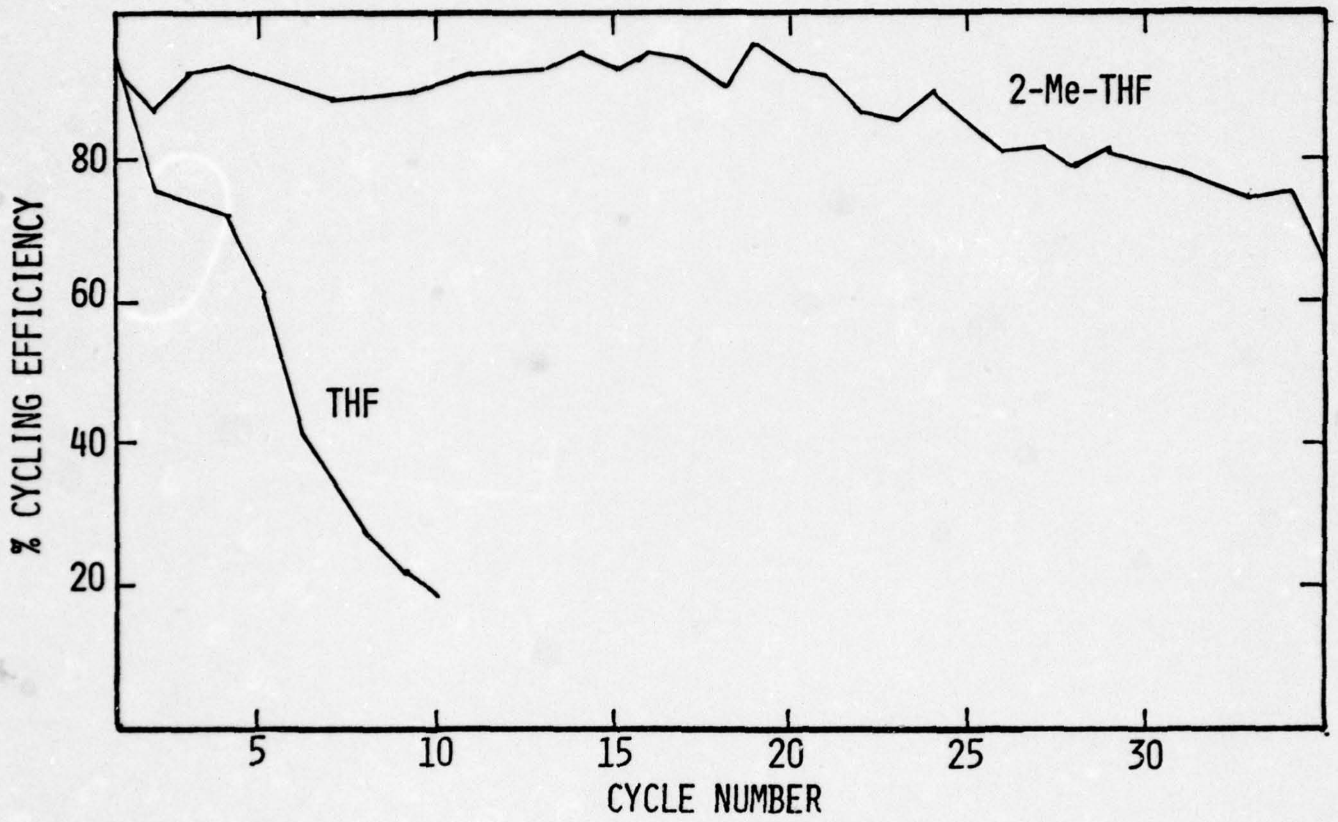


Fig. 1: Efficiencies of cycling Li on a Ni substrate. 1M $LiAsF_6$/cyclic ether; $i_p = i_s = 5$ mA/cm^2; $Q_p = 1.1$ coul/cm^2 (Ref. 6).

That morphology is an important consideration was demonstrated by cycling Li to and from a Li substrate. While cycling efficiencies cannot be ascertained for each individual cycle, an average efficiency ($\bar{E}$) can be calculated. Experimentally, one plates more Li onto the Ni substrate than is stripped on the succeeding cycles. Subsequent cycles proceed at what appears to be 100% efficiency until the excess Li is consumed. For example, if, over the course of 100 1 coul/cm^2 cycles, 1 coul/cm^2 of excess Li is consumed, the average efficiency per cycle is 99%. For 2-Me-THF electrolyte, the Li-on-Li cycling experiment gave $\bar{E}$ values of 96% (1.1 coul/cm^2 plates at 5 mA/cm^2; 3.4 coul/cm^2 excess Li). This value is significantly better than those achieved with electrolytes prepared from $LiAsF_6$ and THF (88%), propylene carbonate (84%) (11), and methyl acetate (60%) (12). Moreover, the average cycling efficiency may be improved by lowering the current density. We observe that $\bar{E}$ increases from 96.0% to 97.4% as i is decreased from 5.0 to 0.9 mA/cm^2.

The cycling behavior of the Li electrode on Li is generally better than on Ni or other substrates. One possible reason for this is that nucleation of the deposit is much easier and, therefore, much more uniform with a Li substrate. Possibly, too, Li is less active as an electrode for the (catalyzed) electrochemical reduction of the solvent than is, say, Ni.

Another test of a solvent's suitability as a Li battery medium is to monitor its reactivity with plated Li on open circuit storage. This technique assesses the intrinsic reactivity of Li with solvent, and the achievement of low reaction rates is a necessary condition for a satisfactory shelf life.

The experiment consists of plating 1.1 coul/cm^2 onto a Ni substrate, and then switching the cell to open circuit (OCV). After a predetermined length of time, the Li plate is electrostripped and the efficiency determined.

Figure 2 compares data obtained from $LiAsF_6$-based THF and 2-Me-THF electrolytes. After 96 hr on OCV, almost 70% of Li plated from the 2-Me-THF electrolyte is seen to be electroaccessible. With THF, however, all of the plated Li is isolated after 48 hr. These data translate into average isolation rates of 1.1 μA/cm^2 (2-Me-THF, 96 hr) and 8.3 μA/cm^2 (THF, 24 hr). At 24 hr, the isolation rate for 2-Me-THF is 1.3 μA/cm^2, almost an order of magnitude lower than that calculated for THF. Data points at 16 and 24 hr appear to be anomalously high and require comment. In all of our work with cyclic ether electrolytes containing $LiAsF_6$, we have observed a recontacting phenomenon whereby some Li lost to encapsulation reactions may be recovered by storage on OCV (9). We believe that this phenomenon also manifests itself in these experiments.

The superiority of 2-Me-THF over THF with regard to inertness towards reduction by Li may be rationalized by the following scheme:

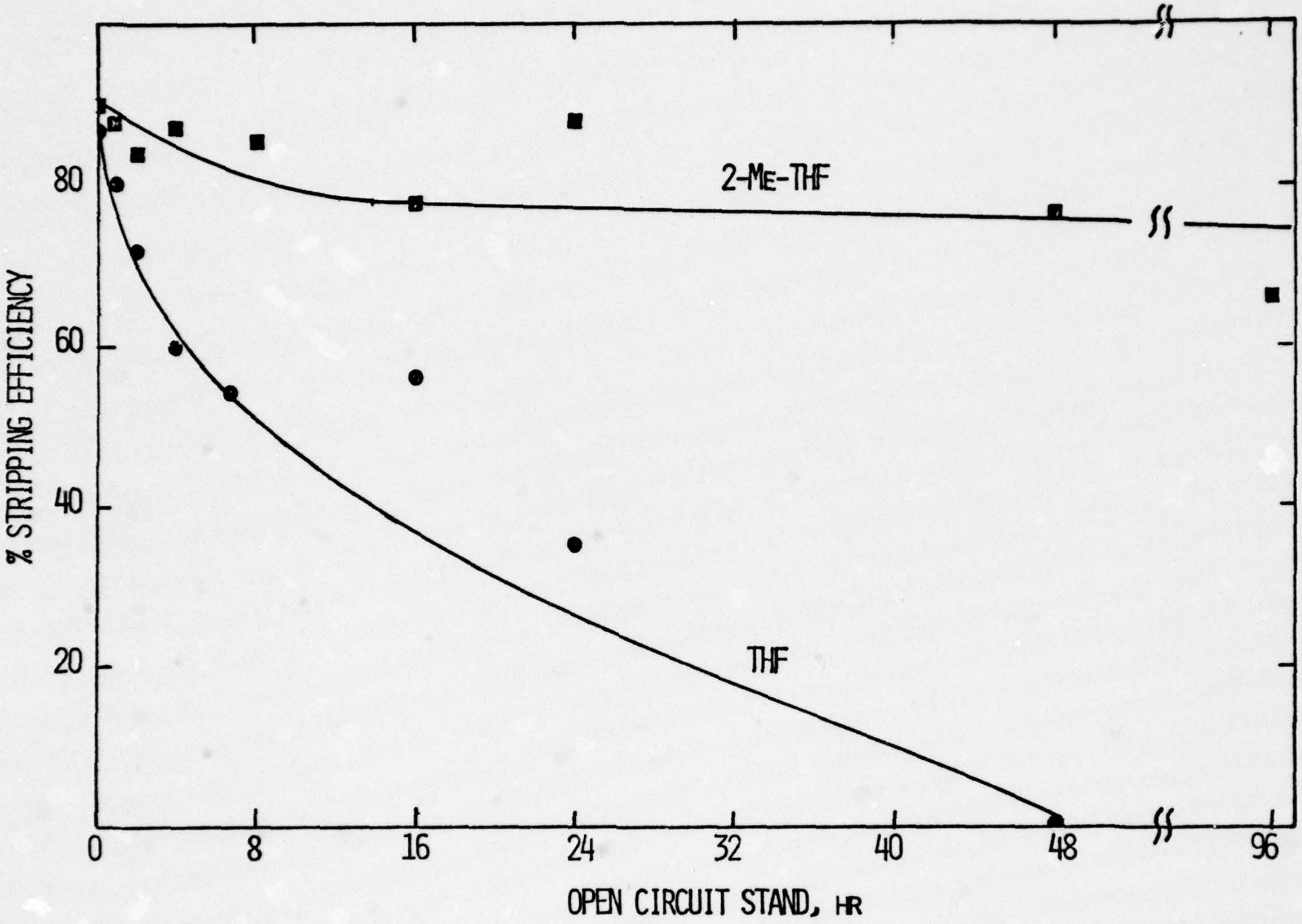
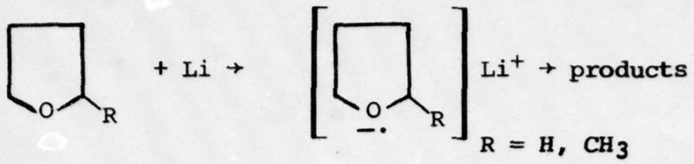


Fig. 2: Stripping efficiencies vs. time on open circuit storage. 1M $LiAsF_6$/cyclic ether; $i_p = i_s = 5$ mA/cm^2; $Q_p = 1.1$ coul/cm^2.



(1)

We propose that THF reacts with Li <u>via</u> a rate-determining one-electron transfer from Li to the lowest unfilled molecular orbital (LUMO) centered on the electronegative oxygen atom. The ease of this transfer is largely determined by the energy of that vacant orbital (13). Thus, by raising the energy of the LUMO, it becomes more difficult to transfer an electron into it.

The energy of the LUMO about the oxygen atom of THF can be perturbed upwards by locating an electron donating group in the 2-position adjacent to the oxygen. The influence of additional electron density on the oxygen atom raises the activation energy required to form the anion-radical. Since a methyl group is known to release electron density through covalent bonds (14), the 2-Me-THF anion-radical becomes more difficult to form. In consonance with this model, preliminary static and dynamic experiments indicate that 3-Me-THF is as reactive as THF, while 2,5-di-Me-THF is at least as inert as 2-Me-THF.

THF is known to undergo reduction <u>via</u> α-proton abstraction by a strong base (15). Thus, a methyl group in the 2-position could conceivably shield one side of the ring from attack. This effectively halves the number of available hydrogens which, in turn, would retard the reaction rate. We do not believe, however, that the large disparity between THF and 2-Me-THF reactivity may be accounted for by the statistical factor alone. Therefore, the LUMO concept of Li-cyclic ether reactivity better accounts for the results at hand, and indicates how suitably functionalized THF molecules may be rendered less reactive towards Li.

On the basis of the static tests at 71°C, the dynamic Li-on-Li cycling experiments at 25°C, and isolation rate studies, it appears that we have the basis for a practical Li electrode. Indeed, preliminary experiments with practical Li charges yield efficiency values comparable to those achieved with 1.1 coul/cm^2 plates. When combined with suitable cathode materials such as transition metal chalcogenides in general (16-20) and TiS_2 (17,18) or a vanadium/transition metal chalcogenide of the form $V_{1-x}M_xS_2$ (M = Fe or Cr) in particular (19), electrolytes based on 2-Me-THF may pave the way to the implementation of a practical Li secondary battery (21).

REFERENCES

1. R. J. Jasinski, High Energy Batteries (Plenum Press, New York, 1967).
2. R. Selim and P. Bro, J. Electrochem. Soc., 121, 1467 (1974); J. Jorné and C. W. Tobias, J. Appl. Electrochem., 5, 279 (1975).
3. R. D. Rauh and S. B. Brummer, Electrochim. Acta, 22, 75 (1977).
4. V. R. Koch and S. B. Brummer, ibid., 23, 55 (1978).
5. J. Butler, D. Cogley and J. Synnott, J. Phys. Chem., 73, 4026 (1969).
6. V. R. Koch, U.S. Patent 4,118,550, October 3, 1978.
7. C. Carvajal, J. J. Tölle, J. Smid and M. Szwarc, J. Am. Chem. Soc., 87, 5548 (1965).
8. D. Nicholls, C. Sutphen and M. Szwarc, J. Phys. Chem., 72, 1021 (1968).
9. V. R. Koch and J. H. Young, J. Electrochem. Soc., 125, 1371 (1978).
10. V. R. Koch, ibid., 126, 181 (1979).
11. R. D. Rauh, T. F. Reise and S. B. Brummer, ibid., 125, 186 (1978).
12. F. W. Dampier and S. B. Brummer, Electrochim. Acta, 22, 1339 (1977).
13. A. Streitweiser, Molecular Orbital Theory for Organic Chemists (Wiley, New York, 1961), pp. 175-6.
14. E. S. Gould, Mechanism and Structure in Organic Chemistry (Holt, Rinehart and Winston, New York, 1959), p. 203.
15. R. B. Bates, L. M. Kroposki and D. E. Potter, J. Org. Chem., 37, 560 (1972).
16. J. Broadhead, in Power Sources 4, D. H. Collins, Ed. (Oriole Press, Newcastle-upon-Tyne, England, 1973); U.S. Patent 3,791,867 (1974).
17. G. L. Holleck and J. R. Driscoll, Electrochim. Acta, 22, 647 (1977).
18. M. S. Whittingham, Science, 192, 1176 (1976); U.S. Patent 4,009,052 (1977).

19. D. W. Murphy, J. N. Carides, F. J. DiSalvo, C. Cros and J. V. Waszczak, Mat. Res. Bull., 12, 825 (1977); U.S. Patent 4,125,687 (1978(.

20. For an excellent review of alkali metal intercalation chemistry, see M. S. Whittingham, Progress in Solid State Chemistry, 12, 1 (1978).

21. Exxon Enterprises presently offers a rechargeable Li-Al/TiS_2 button cell (electrolyte unknown). A minimum of 5 cycles is claimed.

22. The work on THF was supported by NSF-RANN under Grant No. AER75-03779 and by the Office of Naval Research; the work on 2-Me-THF was supported by the Office of Naval Research.

U.S. Patent 4,118,550

APROTIC SOLVENT ELECTROLYTES AND BATTERIES USING SAME

United States Patent [19] [11] **4,118,550**
Koch [45] **Oct. 3, 1978**

[54] **APROTIC SOLVENT ELECTROLYTES AND BATTERIES USING SAME**

[75] Inventor: **Victor R. Koch,** Framingham, Mass.

[73] Assignee: **EIC Corporation,** Newton, Mass.

[21] Appl. No.: **836,731**

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[58] **Field of Search** 429/194, 197, 198, 199, 429/218; 252/62.2, 500, 510, 518

[56] **References Cited**

U.S. PATENT DOCUMENTS

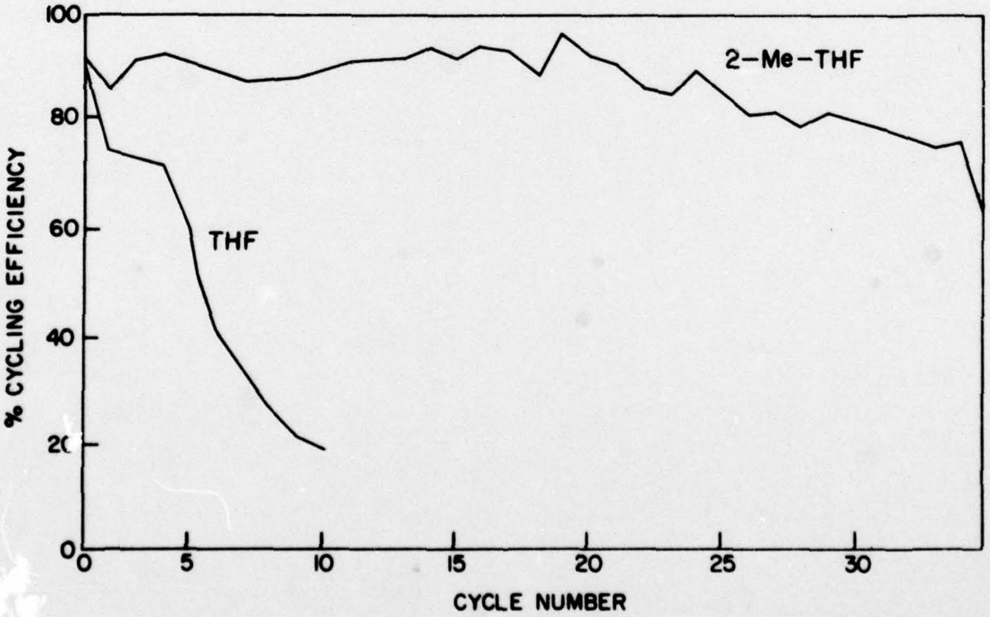
3,701,688	10/1972	Gabano et al.	429/197
3,778,310	12/1973	Garth	429/197
3,877,983	4/1975	Hovsepian	429/194
4,002,492	1/1977	Rao	429/194

Primary Examiner—Charles F. LeFevour
Attorney, Agent, or Firm—Schiller & Pandiscio

[57] **ABSTRACT**

The invention comprises using selected alkylated analogs of tetrahydrofuran and tetrahydropyran as solvents for electrolytes in batteries having alkali metal negative electrodes.

20 Claims, 4 Drawing Figures



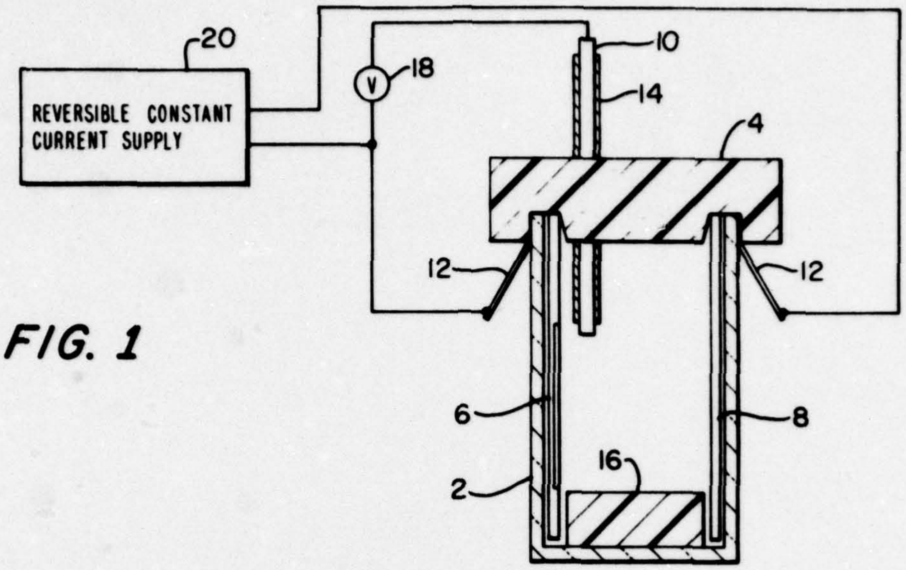

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FIG. 1

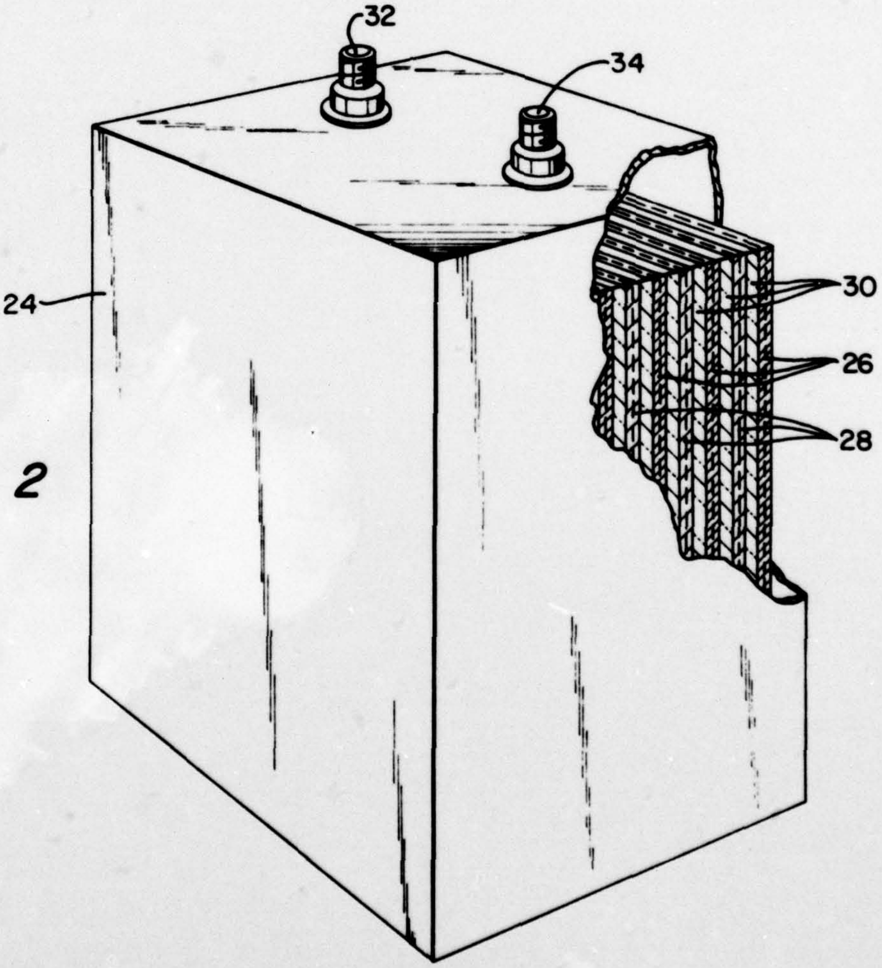
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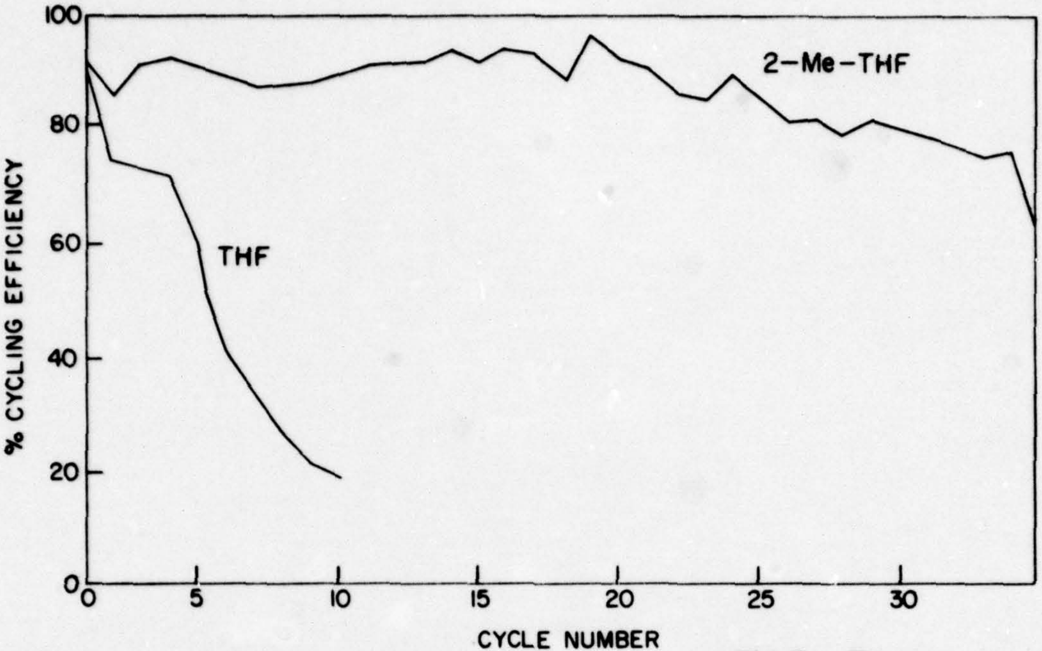
FIG. 2



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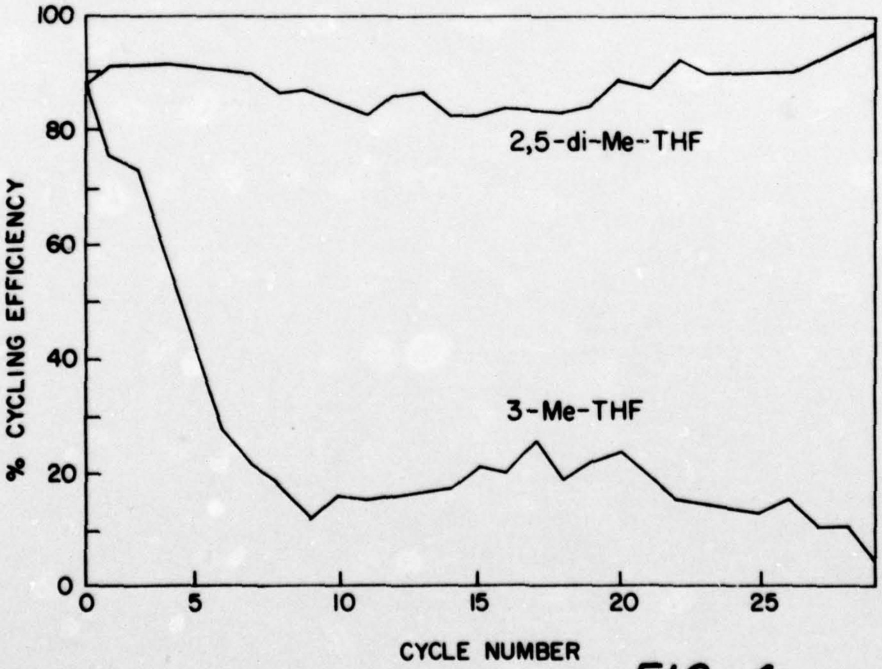
CYCLE NUMBER
2-Me-THF
THF

FIG. 3



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3-Me-THF

FIG. 4

APROTIC SOLVENT ELECTROLYTES AND BATTERIES USING SAME

The Government of the U.S.A. has rights in this invention pursuant to Contract N00014-77-C-0155 awarded by the Department of the Navy.

This invention relates to electrochemical cells and more particularly to improved non-aqueous electrolytes for cells incorporating negative electrodes comprising highly reactive alkali metals, and especially lithium-containing anodes.

Extensive efforts have been expended in developing electrochemical cells with negative electrodes made of lithium and lithium alloys. The primary reason for the interest in lithium as an electrode material is the fact that it is highly electronegative as well as having a low atomic weight, thereby making possible cells with high energy density. Another important consideration is that lithium electrodes are inherently rechargeable. Lithium can be electrodeposited back onto a conducting anode substrate from solutions containing lithium ions. However, the use of lithium electrodes presents certain problems which have severely hampered the development of secondary, i.e., rechargeable, batteries, particularly ambient temperature batteries. For one thing, lithium is highly reactive and this limits the number of potential solvents that may be used for dissolving appropriate lithium salts to form the required electrolyte. Lithium reaction with a solvent in an electrochemical cell is undesirable since it leads to self-discharging and early battery failure. Another problem is that in the usual case where lithium reacts with the organic solvent component of an electrolyte, the reaction leads to formation of a surface film. If the lithium is not plated smoothly, as tends to be the case when individual lithium grains become encapsulated by the film, subsequently plated lithium tends to be deposited in dendritic form, and the formed dendrites provide an increased surface area which promotes further film formation and encapsulation, thereby speeding up rapid deterioration of cycling efficiency and ultimate failure.

One approach to reducing the self-discharging problem has been to alloy the lithium with a less reactive metal such as aluminum. While this lowers the reactivity of the lithium, it also has the adverse affect of increasing the weight of the electrode and making it more positive than a pure lithium electrode. Another more favored approach has been to develop electrolytes where the required salts are dissolved in aprotic organic solvents which do not react readily with lithium. A large number of organic solvents have been suggested and investigated in connection with various types of cells containing lithium electrodes, e.g. cells with different positive electrode materials and/or different electrolyte salts, and cells with and without mechanical separator means between the electrodes.

Cyclic ethers have been proposed as the solvent component of organic electrolyte solutions and heretofore tetrahydrofuran, an aliphatic cyclic ether commonly referred to as THF, has been studied in depth since it has a number of physical and chemical properties which favor its use in a secondary lithium battery. In particular, THF has a wide liquid range (−108° C. to +65° C. at 1 atm.) and low viscosity (0.461 cp. at 25° C.), forms highly conductive solutions of lithium salts, and generally manifests low chemical reactivity. It also has been found to react less readily with lithium than many other solvents that have been studied. Nevertheless the reactivity of THF with respect to lithium is still sufficiently great to render it unsuitable for Li secondary battery applications, and particularly for ambient temperature batteries, i.e., batteries operating in the vicinity of 25° C.

Accordingly, one primary object of this invention is to provide an improved electrolyte for electrochemical cells which comprise an alkali metal negative electrode.

A second primary object is to provide a new and improved electrochemical cell of the type comprising an alkali metal negative electrode.

Another object of the invention is to provide an improved electrolyte for a cell having a lithium-containing electrode which comprises an organic solvent that is substantially more inert than tetrahydrofuran with respect to lithium yet has a conductivity sufficiently great to provide a cell of relatively low internal resistance at ambient temperatures.

Still another object is to provide a "lithium battery" (socalled because its negative electrode material consists of or is predominantly lithium) which is rechargeable, has a high cycling efficiency and high power density at ambient temperatures, and is useable at ambient temperatures.

These objects are attained by providing an aprotic solvent electrolyte which essentially comprises 2-methyltetrahydrofuran (2-Me-THF), 2,5-dimethyltetrahydrofuran (2,5-di-Me-THF), 2-methyltetrahydropyran (2-Me-THP), 2,6-dimethyltetrahydropyran (2,6-di-Me-THP), and higher alkyl homologs of the foregoing.

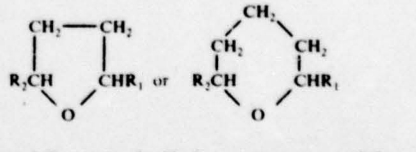
Other features and many of the attendant advantages of the invention are set forth in or made obvious by the following detailed description of the invention which is to be considered together with the accompanying drawings wherein:

FIG. 1 is a schematic view of a half cell used in evaluating the cycling efficiency of Li electrodes in electrolytes made according to this invention;

FIG. 2 is a schematic view of a preferred form of battery incorporating the present invention; and

FIGS. 3 and 4 illustrate cycling efficiencies of THF and THF-homolog electrolytes.

According to this invention an aprotic organic electrolyte is provided in which the solvent comprises or consists of a selected alkyl homolog of tetrahydrofuran (C_4H_8O) or tetrahydropyran ($C_5H_{10}O$). More specifically, the solvent comprises or consists of a heterocyclic compound from one of the following classes of compounds:



where R_1 and R_2 are both alkyl groups or one of them is an alkyl group and the other is hydrogen, said alkyl group being a methyl, ethyl, propyl, isopropyl, butyl, isobutyl or tertiary butyl group.

It has been determined that alkylation of THF, e.g., by addition of a methyl group to form 2-methyltetrahydrofuran tends to have a greater affect on its dielectric constant and specific conductivity than on its density and viscosity. Like THF, 2-methyltetrahydrofuran is liquid over the wide range of terrestial ambient temperatures. However, electrolytes made with 2-Me-THF are substantially less conductive than THF. It appears that the conductivity of the alkylated THF electrolyte varies with the number and location of the alkyl group that is added to the THF nucleus. Thus the conductivity of 1M lithium hexafluoroarsenate ($LiAsF_6$) electrolytes made with 3-methyltetrahydrofuran (3-Me-THF) and 2,5-dimethyltetrahydrofuran are greater and smaller respectively than electrolytes made with 2-Me-THF. All three solvents provide electrolytes with sufficient conductivity to satisfy the requirements of a low rate battery and 2-Me-THF and 3-Me-THF actually have sufficient conductivity for a high rate battery (in this context, a high rate battery is one having a discharge current density of at least 2.5 mA/cm^2).

However, while high conductivity is an important consideration in choosing an electrolyte for a lithium battery, the fundamental criterion in the selection process is stability toward lithium. In this regard it is significant that alkylation of a cyclic ether has an affect on its reactivity with respect to lithium. Thus, there are substantial differences in lithium reactivity among THF, 2-Me-THF, 3-Me-THF, and 2,5-di-Me-THF. Of these, 2-Me-THF and 2,5-di-Me-THF are paramount in lithium stability compared with THF and 3-Me-THF.

The advantages of alkylated electrolyte solvents selected in accordance with this invention are exemplified by the results of static and dynamic tests which were conducted with four selected solvents: THF, 2-Me-THF, 3-Me-THF and 2,5-di-Me-THF. The static tests included exposing electrolytes prepared from the foregoing cyclic ethers (solvent plus $LiAsF_6$ or $LiClO_4$) to lithium by incubating lithium foil with electrolyte at 71° C. (a temperature which in two weeks approximates one year of room temperature storage). The onset of lithium-electrolyte reaction visually manifests itself by corrosion on the lithium foil and concurrent yellowing of the electrolyte. The rate of reaction with lithium was compared from one ether to another and also among various levels of purification for a given ether.

Table I indicates the time of onset of lithium reaction for the four ethers at 71° C. using three different purification procedures identified as A, APA and DAPA. Procedure A involved passing the solvent through activated alumina prior to addition of the electrolyte salt; procedure APA was procedure A followed by pre-electrolysis of the solvent between two lithium electrodes and then another pass through activated alumina; and procedure DAPA involved distilling the solvent on a spinning band column followed by procedure APA.

Table I

Purification Procedure	1M $LiAsF_6$/ THF	1M $LiAsF_6$/ 2-Me-THF	1M $LiClO_4$/ 2-Me-THF	1M $LiAsF_6$/ 3-Me-THF	1M $LiAsF_6$/ 2,5-di-Me-THF
None	2 (16)[a,b]	—	—	—	—
A	25 (28)	>6 Mo.	—	—	—
APA	4 (7)	>6 Mo.	—	—	—
DAPA	—	>1 Mo.	>1 Mo.	10 (4)	>3 Mo.

[a] Observable Li corrosion after 2 days; observable electrolyte coloration after 16 days.

[b] THF (Burdick and Jackson, Distilled-in-glass) was used without further distillation. The APA preparation is equivalent to DAPA for the other solvents.

Referring to Table I, while THF based electrolyte reacts relatively early regardless of purification procedure, 2-Me-THF electrolytes with either $LiAsF_6$ or $LiClO_4$ tend to remain inert toward lithium for as much as six months or more, while 1M $LiAsF_6$/2,5-di-Me-THF is inactive for over three months. However, 3-Me-THF based electrolytes start to react with lithium at substantially the same time as THF based electrolytes. Hence, the results of those static tests show that 2-Me-THF and 2,5-di-Me-THF are far superior to THF and 3-Me-THF as solvents for Li secondary battery applications.

Dynamic testing of electrolytes based on the same four cyclic ethers was achieved by galvanostatically cycling lithium to and from substrates of lithium and nickel at 25° C. ± 2° C., so that a fresh lithium surface came into contact with electrolyte on every cycle. The dynamic testing was accomplished with an experimental half cell as shown in FIG. **1**. The experimental cell consisted of a rectangular glass container **2** (10 × 40 × 60 mm) having a polypropylene cover **4**. Disposed within the container was a flat nickel working electrode **6**, a flat lithium counter electrode **8**, and a lithium foil reference electrode **10**. The nickel working electrode and the lithium counterelectrode were supported by the polypropylene cover and each was provided with a nickel lead **12**. The lithium foil reference electrode was disposed within a glass tube **14** and protruded from the open bottom end of the glass tube as shown. The nickel working electrode and the lithium counter electrode were kept apart and essentially parallel to one another by a polypropylene spacer **16** located at the bottom of the container. The nickel electrode, which measured 5.5 × 3.8 cm and had a thickness of 5 mils, was masked with Teflon tape so as to leave an exposed working area of 9 cm^2. The lithium counter electrode also measured 5.5 × 3.8 cm but had a thickness of 15 mils. A voltmeter **18** was connected across the nickel working electrode and the lithium reference electrode, while a constant current d.c. power supply **20** was connected across the nickel working electrode and the lithium counter electrode. The glass container was filled with an electrolyte consisting of a one molar concentration of lithium hexafluoroarsenate in each of the solvents tested. The galvonostatic cycling was conducted with the same current density for both plating and stripping operations. Lithium-electrolyte reactivity was noted in terms of a loss of cycling efficiency (the ratio of lithium stripped to lithium plated) with increasing cycle number.

FIG. **3** illustrates the cycling efficiencies of the THF and 2-Me-THF electrolytes while FIG. **4** illustrates the cycling efficiencies of 2,5-di-Me-THF and 3-Me-THF electrolytes. In the case of the 2,5-di-Me-THF electrolyte, cycling was conducted at a current density of 0.7 mA/cm^2 and the charge plated (Q_p) was 1.125 coulombs/cm^2, while for the THF, 2-Me-THF and 3-Me-THF electrolytes the current density and charge plated values were 5mA/cm^2 and 1.125 coulombs/cm^2. Although 50–100 coulombs/cm^2 would normally be cycled in a practical, i.e., commercial cell, thin plates are useful in rapidly assessing the quality of a given electrolyte since cycling of thin plates many times exacerbates conditions leading to inefficiencies and electrode failure. In the test results illustrated in FIG. 3, on the 10th cycle run in THF-based electrolyte, about 75% of the lithium plated is encapsulated by films and lost to anodic dissolution. By comparison, only about 7% of lithium plated from 2-Me-THF based electrolyte is electrically isolated. While the electrolyte does degrade with cycle number, as evidenced by decay of cycling efficiency, the results represented by FIG. 3 clearly demonstrate that a 2-Me-THF based electrolyte provides a substantial and unexpected improvement in cycling efficiency in comparison to a THF-based electrolyte with identical solute and solute concentrations. FIG. 4 illustrates that 3-Me-THF behaves very much like THF in terms of cycling efficiency. In contrast, the di-methylated solvent manifested very good cycling efficiencies, albeit at low current densities. The 2,5-di-Me-THF electrolytes has substantially less conductivity than 3-Me-THF. The specific conductance of 1M $LiAsF_6$/2,5-di-Me-THF electrolyte at 25° C. is 0.19×10^{-3} $(ohm\ cm)^{-1}$ compared to 7.4×10^{-3} $(ohm\ cm)^{-1}$ for 1M $LiAsF_6$/3-Me-THF, about 13.0×10^{-3} $(ohm.\ cm)^{-1}$ for THF and about 3.0×10^{-3} $(ohm.\ cm)^{-1}$ for 2-Me-THF. Thus, while the dimethylated solvent affords good stability toward lithium at temperatures in the order of 70° C. and good cycling efficiency, its poor conductivity precludes its use as the sole solvent in a high rate battery, i.e., a battery having a discharging current density of 2.5 mA/cm^2 or greater.

While $LiAsF_6$ is the preferred ionic conductor solute for electrolytes made in accordance with this invention, lithium perchlorate is preferred as a second choice.

It is believed that the superior stability of 2-Me-THF and 2,5-di-Me-THF in contrast to THF and 3-Me-THF is due to the location of a methyl group in the 2-position of the oxolane ring. Alkyl groups (methyl, ethyl, propyl, etc.) are known to manifest positive inductive effects, i.e., they release electron density through covalent bonds. Thus, a methyl group in the 2-position (or methyl groups in the 2,5-positions) would be expected to raise the activation energy of the electron transfer reaction whereby an electron is transferred from lithium to the lowest unfilled molecular orbital (LUMO) centered on the electronegative oxygen atom of the oxolane ring. A similar group in the 3 position would be expected to have little effect on the LUMO since inductive effects are rapidly attenuated through saturated carbon-carbon bonds. Thus, 3-Me-THF and THF would be expected to behave similarly with respect to lithium, while 2-Me-THF and 2,5-di-Me-THF would be expected to show far less lithium reactivity. Similar behavior can be expected of 2-Me-THP and 2,6-di-Me-THP, and other higher alkyl homologs of THF and THP where the methyl group(s) is(are) replaced by other alkyl groups such as ethyl, propyl, isopropyl, butyl, isobutyl and tertiary butyl groups so as to give, for example, 2-ethylTHF, 2-ethylLTHP, 2,5-diethylTHF, 2,6-diethylTHP, etc. Alkylating THF or THP with alkyl groups having 5 or more carbons is not practical for cost and weight considerations.

For a high energy density ambient temperature battery embodying this invention, the negative electrode material preferably consists of lithium of as high purity as possible. Nevertheless, for certain other battery applications it may consist of a lithium alloy or amalgam. If a lithium alloy is used, it preferably is a lithium-tin, lithium-lead, lithium-gold, lithium-platinum, lithium-cadmium, lithium-mercury, lithium-zinc, lithium-silver, lithium-aluminum or lithium-magnesium alloy having at least about 63% lithium by weight. However, alloys having a smaller percentage of lithium may be satisfactory in certain cases.

For a high energy density ambient temperature battery, the positive electrode material preferably consists of titanium disulfide (TiS_2). Preferably this positive electrode material is made in accordance with the teachings of U.S. Pat. No. 4007055, issued Feb. 8, 1977 to M. Stanley Whittingham, or U.S. Pat. No. 3980761, issued Sept. 14, 1976 to Arthur H. Thompson et al. However, for other less stringent battery applications the positive electrode material may comprise other transition metal compounds and notably other insoluble chalcogenides (as for example mentioned in U.S. Pat. Nos. 4002492, 4007055 and 4009052) of titanium, zirconium, hafnium, vanadium, niobium, tantalum, molybdenum, tungsten, rhenium, platinum, germanium, iron, tin and lead, e.g., TiS_3, $TiSe_2$, $TiSe_3$, ZrS_2, ZrS_3, HfS_2, HfS_3, VS_2, VS_3, NbS_2, NbS_3, TaS_2, TaS_3, $ZrSe_2$, $ZrSe_3$, $HfSe_2$, $HfSe_3$, VSe_2, VSe_3, $NbSe_2$, $NbSe_3$, $TaSe_2$, $TaSe_3$, and alloys of the foregoing cations such as $ZrHfSe_2$. Other positive electrode materials may comprise mixed sulfides such as $Fe_xV_{1-x}S_2$ and $Cr_xV_{1-x}S_2$ $(x<1)$ and sulfide compounds such as $NiPS_3$ and metal oxides such as MoO_3, V_2O_5 and Cr_xO_y where y/x is between 1.5 and 3. Soluble and partially soluble positive electrode materials also may be used, notably I_2, Br_2, Cl_2, SO_2, S, CuCl, $CuCl_2$, AgCl, $FeCl_2$, $FeCl_3$, and other transition metal halides. Other soluble positive electrode materials that may be used are lithium polysulfide (Li_2S_n) and organic compounds such as chloranil and fluoranil. In the case of Li_2S_n, it is preferred that n be approximately 10. Titanium disulfide is the preferred positive electrode material because of electrical, weight and cost consideration.

Preferably the cathode structure consists of the positive electrode material deposited on a suitable substrate such as carbon, nickel, zinc, etc., but the cathode structure may consist entirely of the positive electrode material where the latter is capable of serving as its own current collector. A preferred cathode structure consists of titanium disulfide mixed with carbon and pressed onto a nickel substrate. In the case where the positive electrode material is soluble in the electrolyte to a significant extent, e.g., lithium polysulfide, any suitable electronic conductor which is not soluble in or reactive with the electrolyte may be used as the cathode current collector, e.g. carbon or nickel or carbon in a plastic matrix such as Teflon or polyethylene.

The concentration of the solute (ionic conductor) in the solvent is not critical. It is preferred to incorporate the minimum amount sufficient to yield the desired level of conductivity when the cell is fully charged. By way of example, the salt concentration should be such as to preferably give a specific conductivity of at least about 5×10^{-5} $ohm^{-1}cm^{-1}$ at about 22° C. In practice, a 1.0 to 2.5 M concentration of solute in the solvent generally will provide a suitable level of ionic conductivity.

The solute is a compound which is ionically dissociable in the electrolyte solvent and may consist solely of an ionizable soluble salt whose cation is of the same metal (lithium) as the negative electrode material. The solute may consist solely of such a lithium compound, and cells using electrolytes made according to this invention with a lithium compound as the sole ionic conductor will function satisfactorily. However, if the solute has an anion component the same as that of the positive electrode, it is subject to the disadvantage that if the cell is overcharged the solute may be substantially depleted from the electrolyte, thereby adversely affecting its conductivity. Accordingly, it is preferred to use a solute with an anion different from that of the positive electrode, e.g., lithium hexafluoroarsenate or perchlorate, when the positive electrode is titanium disulfide. Alternatively, the solute may comprise any soluble lithium salt such as tetrabromoaluminate ($LiAlBr_4$), lithium thiocyanate, lithium tetrachloroaluminate ($LiAlCl_4$) lithium tetrafluoroborate, lithium bromide, lithium hexafluorophosphate, and lithium salts of organic acids such as trichloroacetic, trifluoromethanesulfonic, and formic acids.

In constructing practical cells in accordance with this invention, it is preferred that the positive and negative electrode members be formed as flat plates or foils and pressed together against a suitable non-conductive porous separator which has pores large enough to be permeable to the electrolyte. However, the invention also is applicable to cells where the positive and negative electrodes are widely spaced from one another with or without intervening separator means.

FIG. 2 illustrates a form of rechargeable single cell battery incorporating a preferred embodiment of the invention. The illustrated battery comprises a sealed battery case **24** within which is disposed a plurality of flat negative electrodes **26** consisting of essentially pure lithium deposited on nickel substrates, a plurality of flat positive electrodes **28** consisting of titanium disulfide deposited on expanded nickel, and a plurality of separators **30** in the form of flat porous mats made of microporous polypropylene film (Celgard) or glass fibers. The positive and negative electrodes are arranged alternatively with one another and a separator is disposed between each pair of positive and negative electrodes. Surrounding the array of electrodes and separators and filling the interstices of the separators is an electrolyte (not shown) which consists of a 1 molar solution of lithium hexafluoroarsenate in 2-methyl-tetrahydrofuran. The positive electrodes of the several cells are electrically coupled in parallel to a positive terminal **32** by suitable electrical conductors (not shown) in accordance with conventional battery fabrication technology, and the negative electrodes of the several cells are similarly connected to a negative battery terminal **34**. The resulting single cell is rechargeable and has an open cell voltage of about 2.7 volts when fully charged, and is capable of being used at temperatures between about −40° C. to about 150° C. Such a cell may be constructed so as to qualify as a high rate battery and has the advantage of having a longer shelf life than lithium batteries in which THF is the electrolyte solvent. Of course several such cells may be connected in series so as to provide a battery of higher voltage.

The liquid range of 2-Me-THP is displaced to higher values by approximately 20° when compared to 2-Me-THF, i.e., −6° to 102° C. for the former; −137° to 80° C. for the latter. To achieve low temperature operation with electrolytes composed of higher molecular weight cyclic ethers, diluents such as 1,2-dimethyloxyethane (DME), THF, and/or diethylether could be added. The role of a diluent is to maintain fluidity and ionic conductivity by lowering the viscosity. At temperatures near or at the boiling points of these solvents sealed cans would be employed.

It is to be understood that the invention is susceptible of a number of obvious modifications. Thus the electrolyte may comprise a mixture of solvents including THF or THP, e.g., a mixture of 2-Me-THF and 2-Me-THP or a mixture of either of them with THP or THF. Also electrolytes made in accordance with this invention may be used in cells where the anode essentially includes or is a material other than lithium, e.g., potassium, sodium, magnesium, calcium or zinc, or a mixture thereof with or without lithium. Furthermore while the invention is most advantageous in providing high energy density secondary cells, the electrolyte may be formulated so as to provide stable low or medium energy density cells. Still other modifications and advantages will be obvious to persons skilled in the art.

What is claimed is:

1. An electrochemical cell comprised of:

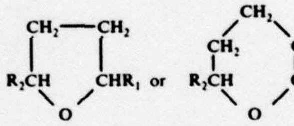
positive and negative electrodes with said negative electrode comprising lithium; and

an electrolyte providing an ionically conductive path between said electrodes comprised of an ionically dissociable lithium salt and a solvent for said salt consisting of a compound from the class consisting of 2-methyltetrahydrofuran, 2,5-dimethyltetrahydrofuran, 2-methyltetrahydropyran, 2,6-dimethyltetrahydropyran, and higher alkyl homologs thereof.

2. A rechargeable electrochemical cell comprising:

positive and negative electrodes with said negative electrode consisting essentially of lithium as the active electrode materal; and

an electrolyte providing an ionically conductive path between said electrodes, said electrolyte comprising an ionically dissociable lithium salt and a solvent for said salt which is primarily one or more compounds represented by the formula



where R_1 and R_2 are both alkyl groups or one of them is an alkyl group and the other is hydrogen, said alkyl group being a methyl, ethyl, propyl, isopropyl, butyl, isobutyl or tertiary butyl group.

3. A cell according to claim **2** where the solvent comprises 2-methyltetrahydrofuran.

4. A cell according to claim **3** wherein the solvent consists of 2-methyltetrahydrofuran.

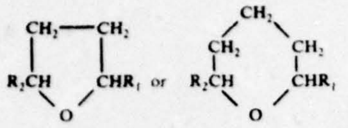
5. A cell according to claim **4** wherein the solvent consists of 2,5-dimethyltetrahydrofuran.

6. A cell according to claim **2** where the solvent comprises 2,5-dimethyltetrahydrofuran.

7. A rechargeable cell according to claim **2** in which the positive electrode is titanium disulfide or a lithium polysulfide.

8. A cell according to claim **2** wherein the solute is a lithium salt other than lithium perchlorate.

9. An electrolyte for use in an electrochemical cell having a lithium negative electrode, said electrolyte comprising an ionically dissociable solute in the form of a lithium salt and a solvent for said salt which comprises predominantly one or more members from the class consisting of compounds conforming to the formula



where R_1 and R_2 are both alkyl groups or one of them is an alkyl group and the other is hydrogen, said alkyl group being a methyl, ethyl, propyl, isopropyl, butyl, isobutyl or tertiary butyl group.

10. An electrolyte according to claim **9** where the solvent comprises 2-methyltetrahydrofuran.

11. An electrolyte according to claim **9** where the solvent comprises 2,5-dimethyltetrahydrofuran.

12. An electrolyte according to claim **9** where the solvent comprises only one cyclic ether, and that one cyclic ether is either 2 methyltetrahydrofuran or 2,5-dimethyltetrahydrofuran.

13. An electrolyte according to claim **12** where the solute consists of or comprises lithium perchlorate.

14. An electrolyte according to claim **12** where the solute consists of or comprises lithium hexafluoroarsenate.

15. An electrolyte according to claim **6** where the solute consists of or comprises one of the following: lithium hexafluorophosphate, lithium perchlorate, lithium hexafluoroarsenate, lithium tetrachloroaluminate, lithium bromide, lithium tetrafluoroborate, lithium tetrabromoaluminate, lithium thiocyanate, and lithium salts of trichloroacetic, trifluoroacetic, trifluoromethanesulfonic, and formic acids.

16. An electrolyte according to claim **15** wherein the solvent includes at least one of the following compounds: tetrahydrofuran, tetrahydropyran, 1,2-dimethyloxyethane and diethylether.

17. An electrolyte according to claim **16** wherein the solvent comprises 2-methyltetrahydrofuran and at least one of the following: tetrahydrofuran, 1,2-dimethyloxyethane, diethylether and tetrahydropyran.

18. An electrolyte according to claim **16** wherein the solvent comprises 2,5-dimethyltetrahydrofuran and at least one of the following: tetrahydrofuran, 1,2-dimethyloxyethane, diethylether and tetrahydropyran.

19. An electrolyte according to claim **9** wherein the solute consists of or comprises one of the following: lithium hexafluorophosphate, lithium hexafluoroarsenate, lithium tetrachloroaluminate, lithium bromide, lithium tetrafluoroborate, lithium tetrabromoaluminate, lithium thiocyanate, and lithium salts of trichloroacetic, trifluoroacetic, trifluoromethanesulfonic, and formic acids.

20. An electrolyte according to claim **19** wherein the solvent consists of either or both members of the group consisting of 2-methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran.

* * * * *

IV. FURTHER WORK

Research on the methylated THFs suggests that suitably functionalized oxolane rings are more resistant to reduction than THF alone. To distinguish between this possibility and the intervention of adherent Li^+ permeable films, we plan on establishing an intrinsic reactivity order of solvents towards Li in the absence of films. To this end, THF and the methylated THFs will be incubated with Li amalgam and the rate of Li^+ generation monitored by atomic absorption (AA) spectroscopy.

Since $LiAsF_6$ is reactive towards Li (as described in Technical Report No. 01), we will continue to search for alternative Li salts. Likely candidates are $LiAlOCl_3$ and $Li_2Al_2OCl_6$.

Finally, we plan on extending the Li cycling experiments in the direction of practical Li plates, i.e., 50-100 coul/cm^2. Cycling efficiencies as a function of current density, temperature and plate thickness will be assessed.

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