

logic materials (10). Thus, by the time acid rain first appears as stream flow (site I), its acidity has already been greatly diminished, going from 72 μeq of H^+ per liter of average acid rain (2) to 18 μeq /liter (site I in Table 1). Subsequently, further neutralization of the strong acids is effected by chemical weathering reactions with the concurrent loss of dissolved aluminum and the gain of strong bases and silica by the coexisting water (Table I and Fig. 2B). This aged water is in equilibrium with kaolinite and typifies one of the principal water types at Hubbard Brook (11).

Falls Brook is not unique with respect to its distribution of acidity and ion chemistry. The main tributary of Falls Brook (Fig. 1) and another low-order, low-elevation drainage system (Little Brook in Fig. 1) have also been monitored periodically along their lengths. These streams show a pattern of downstream chemical change identical in kind to that obtained in Falls Brook. It appears that the observed chemical changes are not a function of elevation within the watershed but rather a function of stream order, irrespective of elevation. Similarly, investigators have sampled stream networks draining a variety of igneous and metamorphic rock types in New Hampshire and Vermont (12). A pattern of diminishing acidity in the downstream direction has been observed in every case. Falls Brook thus appears to be representative of a more general regional process and effect.

We may thus reasonably infer that the neutralization of acid rain over the granitic and forested terrane of New England is accomplished in low-order watersheds by the two-step chemical process described above. The presence of high concentrations of dissolved aluminum has been reported for acidified waters from a variety of environments including the alpine zone of New Hampshire (13), the Adirondack region (9), and Norway (14). As long as strong acids persist in solution, the neutralization reactions proceed essentially as a base exchange reaction at constant ionic strength (Fig. 2). However, when the strong acids are eventually neutralized, carbonic acid will ionize and the ionic strength of the system may increase through open-system carbonation reactions.

Some of the more general implications of this mode of acid rain neutralization include the following:

1) Hydrologically, the effect of acid rain on stream water quality will be evident mainly in low-order drainage systems, especially where the bedrock is chemically unreactive as in an igneous

and metamorphic terrane. In the marble belts of New England, acid rain neutralization is rapidly accomplished by the solution of carbonate minerals (15). Probably no sustained acidifying effect will be manifested on major streams, regardless of bedrock type.

2) As a consequence, lakes whose watersheds are composed of igneous or metamorphic bedrock and which receive water from low-order streams will tend to be acidified and rich in aluminum. In general, it may be anticipated that alpine and upland lakes will show this effect more than lowland lakes or those that receive mostly aged stream water or groundwater, or both.

3) With respect to soils, the participation of soil aluminum in the immediate acid neutralization process probably dislocates or otherwise disturbs the normal order of soil formation (13). The soil and regolith of the New England landscape are presently acting as a large sump for the absorption of excess strong acidity.

4) Geologically, no excessive chemical weathering activity can be attributed to acid rain over the northeastern United States. The contemporary ionic denudation rate of New England (0.22 eq/m^2) is well below the North American average (0.38 eq/m^2), despite the added component of strong acids washing out over New England (2, 3).

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References and Notes

- G. E. Likens and F. H. Bormann, *Science* **184**, 1176 (1974); G. E. Likens, N. M. Johnson, J. N. Galloway, F. H. Bormann, *ibid.* **194**, 643 (1976); G. E. Likens, *Chem. Eng. News* **54**, 29 (1976).
- G. E. Likens et al., *Biogeochemistry of a Forested Ecosystem* (Springer-Verlag, New York, 1977).
- N. M. Johnson, R. C. Reynolds, G. E. Likens, *Science* **177**, 514 (1972).
- G. E. Likens, F. H. Bormann, N. M. Johnson, R. S. Pierce, *Ecology* **48**, 772 (1967); D. N. Fisher, A. M. Gambell, G. E. Likens, F. H. Bormann, *Water Resour. Res.* **4**, 115 (1968). Aluminum is analyzed by a colorimetric ferrozine-orthophenanthroline technique after samples are digested in acid. Ionized carbonic acid is determined by the difference between the pH of the initial sample and the pH after CO_2 has been purged from the system.
- C. J. Lind and J. D. Hem, *U.S. Geol. Surv. Water Supply Pap.* 1827-G (1975); W. C. Graustein, K. Cromack, Jr., P. Sollins, *Science* **198**, 1252 (1977).
- Because no crystalline gibbsite has been detected in Hubbard Brook soils (R. C. Reynolds, personal communication), the solubility product for amorphous (microcrystalline) gibbsite has been used as reported by J. D. Hem and C. E. Robertson [U.S. Geol. Surv. Water Supply Pap. 1827-A (1967)]. However, other basic aluminum salts may be involved as suggested by C. R. Frick and by N. van Breeman in papers presented at the International Symposium on Acid Sulfate Soils, International Institute for Land Reclamation and Improvement, Wageningen, Netherlands, 1973.
- R. M. Garrels and C. L. Christ, *Solutions, Minerals and Equilibria* (Harper and Row, New York, 1965).
- J. E. Hobbie and G. E. Likens, *Limnol. Oceanogr.* **18**, 734 (1973); W. McDowell, personal communication.
- C. J. Driscoll, data presented at the Workshop on Limnological Aspects of Acid Precipitation, Sagamore Conference Center, Raquette Lake, N.Y., 25 to 28 September 1978.
- J. S. Eaton, G. E. Likens, F. H. Bormann, *J. Ecol.* **61**, 495 (1973).
- N. M. Johnson, G. E. Likens, F. H. Bormann, D. N. Fisher, R. S. Pierce, *Water Resour. Res.* **5**, 1353 (1969).
- Chemical data from Grant Brook and Mousely Brook (Mount Cube quadrangle, New Hampshire) by R. McGirr and A. Anella; from Mink Brook (Mascoma quadrangle, New Hampshire) by E. Erler and E. Keefauver; from the Ammonoosuc and Pemigewasset rivers, New Hampshire, by K. Dracutt; and from first-order streams in the Vermont marble belt by B. Bishop are given in unpublished reports held by the Earth Sciences Department, Dartmouth College, Hanover, N.H.
- C. S. Cronan, W. A. Reiners, R. C. Reynolds, Jr., G. E. Lang, *Science* **200**, 309 (1978).
- E. T. Gjessing, A. Henrikson, M. Johannessen, R. F. Wright, in *Impact of Acid Precipitation on Forest and Freshwater Ecosystem in Norway*, F. H. Brække, Ed. (SNSF Project Research Report FR6/76, Oslo, Norway, 1978).
- Data of B. Bishop [see (12)].
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2-Methyltetrahydrofuran-Lithium Hexafluoroarsenate:

A Superior Electrolyte for the Secondary Lithium Electrode

Abstract. Rechargeable, high energy density lithium batteries require an efficient lithium electrode. Earlier work with electrolytes based on propylene carbonate, methyl acetate, and tetrahydrofuran yielded poor lithium electrode cycling efficiencies because of electrolyte reduction by lithium. Solutions of lithium hexafluoroarsenate in 2-methyltetrahydrofuran are found to be remarkably stable toward lithium, resulting in cycling efficiencies that approach 98 percent. The ability of 2-methyltetrahydrofuran to resist reduction by lithium is thought to be based on the position of its lowest unfilled molecular orbital relative to that of tetrahydrofuran.

The development of an ambient temperature secondary battery employing a Li negative has been actively pursued over the past 20 years (1). The key tech-

nical problem precluding the implementation of such batteries is the cycling behavior of the Li electrode. Metallic Li can be plated from organic media con-

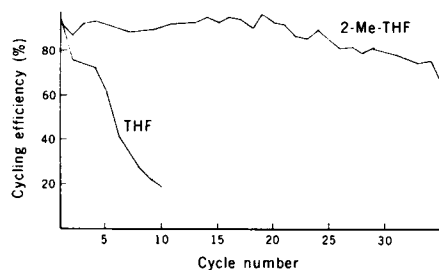


Fig. 1. Efficiencies of cycling Li on a Ni substrate. The electrolyte was 1M LiAsF₆ in cyclic ether; plating current i_p = stripping current i_s = 5 mA/cm²; charge plated Q_p = 1.1 C/cm² (6).

taining Li⁺ ions onto a conducting substrate with 100 percent efficiency (2). However, anodic dissolution of the reactant is invariably less than 100 percent 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 proceed 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 is compounded over several cycles, leading to ultimate electrode failure.

A well-behaved Li electrode is contingent on the development of a medium kinetically, if not thermodynamically, inert toward 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 report, we compare solutions of LiAsF₆ in tetrahydrofuran (THF) and 2-Me-THF in terms of their physical properties and relative inertness toward Li.

At 25°C, the density and viscosity values for 2-Me-THF correspond closely to those of THF: 0.880 g/cm³ and 0.461 cP (7) compared to 0.848 g/cm³ and 0.457 cP (8), respectively. However, the addition of a methyl group alpha to the oxygen atom of THF seriously affects solution conductivity. The specific conductance at 25°C of 1M LiAsF₆ in 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 note that the conductivities (1M LiAsF₆, 25°C) of electrolytes made with 3-Me-THF and 2,5-di-methyltetrahydrofuran (2,5-di-Me-THF) straddle that for 2-Me-THF (7.4×10^{-3} and 0.2×10^{-3} ohm⁻¹ cm⁻¹, respectively), which is consistent with this model. Accordingly, the use of electrolytes comprising alkylated THF's may be restricted to low-rate (< 10 mA/cm²) battery applications. Although high conductivity is an important consideration in choosing an electrolyte, the fundamental criterion in the selection process is stability toward Li, and in this regard 2-Me-THF is a step forward.

The stability of these cyclic ethers toward Li was assessed under static and dynamic conditions. Static tests involved the incubation of Li foil with electrolyte at 71°C. The onset of a Li-electrolyte reaction is seen as 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. Lithium-electrolyte reactivity was noted in terms of a loss of cycling efficiency (defined as charge stripped divided by charge plated) with increasing cycle number.

Static tests revealed that 2-Me-THF distilled from benzophenone ketyl and sealed in Pyrex showed no visible sign of reaction over a 10-month storage period. Similarly treated THF reacted with Li in just 3 days, and whereas solutions of LiAsF₆ and 2-Me-THF were stable over a 13-month period, LiAsF₆-THF media reacted after 25 days. Presumably, impurities introduced by the LiAsF₆ 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. Good cycling efficiency can be achieved only if the electrolyte is kinetically stable to Li. This requires an absence of reactive impurities as well as the chemical compatibility of salt and

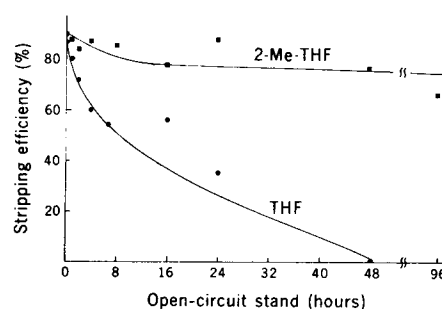


Fig. 2. Stripping efficiencies versus time on open-circuit storage. The electrolyte was 1M LiAsF₆ in cyclic ether; i_p = i_s = 5 mA/cm²; Q_p = 1.1 C/cm².

solvent toward Li. In Fig. 1, the cycling efficiencies of THF and 2-Me-THF electrolytes on Ni are presented as a function of cycle number for 1.1 C/cm² Li plates. (Although 50 to 100 C/cm² of Li would nominally be cycled in a practical cell, thin plates are useful in rapidly assessing the quality of an electrolyte. Cycling of thin plates many times exacerbates conditions leading to inefficiencies and electrode failure.) On the tenth cycle run in THF-based electrolyte, 80 percent of the Li plated is encapsulated by films and lost to anodic dissolution. By comparison, only 7 percent 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 or a very slow reaction of 2-Me-THF with Li yields products that perturb the morphology of subsequent plates.

That morphology is an important consideration was demonstrated by cycling Li to and from a Li substrate. Cycling efficiencies cannot be ascertained for each cycle, but 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 percent efficiency until the excess Li is consumed. For example, if, over the course of 100 1 C/cm² cycles, 1 C/cm² excess Li is consumed, the average efficiency per cycle is 99 percent. For 2-Me-THF electrolyte, the Li-on-Li cycling experiment gave an \bar{E} value of 96 percent (1.1 C/cm² plates at 5 mA/cm²; 3.4 C/cm² excess Li). This value is significantly better than those achieved with electrolytes prepared from LiAsF₆ and THF (88 percent), propylene carbonate (84 percent) (11), and methyl acetate (60 percent) (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

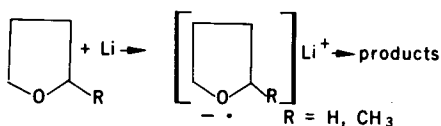
percent as current density is decreased from 5.0 to 0.9 mA/cm².

The cycling behavior of the Li electrode is generally better on Li than on Ni or other substrates. One possible reason for this is that the deposit is nucleated much more easily and is therefore much more uniform with a Li substrate. Lithium may also be 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 its reactivity with plated Li on open-circuit storage. This 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 C/cm² onto a Ni substrate, and then switching the cell to open circuit. After a predetermined time, the Li plate is electrostripped and the efficiency determined.

Figure 2 compares data obtained from LiAsF₆-based THF and 2-Me-THF electrolytes. After 96 hours on open circuit, almost 70 percent of Li plated from the 2-Me-THF electrolyte is electroaccessible. With THF, however, all of the plated Li is isolated after 48 hours. These data translate into average isolation rates of 1.1 μA/cm² (2-Me-THF, 96 hours) and 8.3 μA/cm² (THF, 24 hours). At 24 hours, the isolation rate for 2-Me-THF is 1.3 μA/cm², almost an order of magnitude lower than that calculated for THF. Data points at 16 and 24 hours appear to be anomalously high and require comment. In all of our work with cyclic ether electrolytes containing LiAsF₆, we have observed a recontacting phenomenon whereby some Li lost to encapsulation reactions may be recovered by storage on open circuit (9). We believe that this occurs in these experiments.

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



We propose that THF reacts with Li by 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 upward 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, whereas 2,5-di-Me-THF is at least as inert as 2-Me-THF.

Tetrahydrofuran is known to undergo reduction via alpha 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 toward 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 C/cm² plates. When combined with suitable cathode materials such as transition metal chalcogenides in general (16-20) and TiS₂ (17, 18) or a vanadium-transition metal

chalcogenide of the form V_{1-x}M_xS₂ (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).

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References and Notes

1. R. J. Jasinski, *High Energy Batteries* (Plenum, New York, 1967).
2. R. Selim and P. Bro, *J. Electrochem. Soc.* **121**, 1467 (1974); J. Jorne 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, J. Synnott, *J. Phys. Chem.* **73**, 4026 (1969).
6. V. R. Koch, U.S. patent 4,118,550 (1978).
7. C. Carvajal, J. J. Tölle, J. Smid, M. Szwarc, *J. Am. Chem. Soc.* **87**, 5548 (1965).
8. D. Nicholls, C. Sutphen, 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, S. B. Brummer, *ibid.* **125**, 186 (1978).
12. F. W. Dampier and S. B. Brummer, *Electrochim. Acta* **22**, 1339 (1977).
13. A. Streitwieser, *Molecular Orbital Theory for Organic Chemists* (Wiley, New York, 1961), pp. 175-176.
14. E. S. Gould, *Mechanism and Structure in Organic Chemistry* (Holt, Rinehart & Winston, New York, 1959), p. 203.
15. R. B. Bates, L. M. Kroposki, D. E. Potter, *J. Org. Chem.* **37**, 560 (1972).
16. J. Broadhead, in *Power Sources 4*, D. H. Collins, Ed. (Oriole, 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**, 1126 (1976); U.S. patent 4,009,052 (1977).
19. D. W. Murphy *et al.*, *Mater. 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, *Prog. Solid State Chem.* **12**, 1 (1978).
21. Exxon Enterprises offers a rechargeable Li-Al/TiS₂ button cell (electrolyte unknown). A minimum of five cycles is claimed.
22. The work on THF was supported by NSF-RANN grant AER75-03779 and the Office of Naval Research; the work on 2-Me-THF was supported by the Office of Naval Research.

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Cement Line Motion in Bone

Abstract. Compact bovine bone subjected to constant torsional load for long periods of time exhibits large anelastic effects. Displacements occur at the cement lines and are responsible for part or all of the long-term deformation. The absence of an asymptotic creep strain is consistent with an interpretation of the cement line as a viscous interface.

The present investigation demonstrates that large anelastic deformations occur in specimens of bone loaded in torsion for long periods, that displacements occur at the cement lines, and that these displacements appear to be responsible for much of the time-dependent deformation. The results constitute the first clear experimental evidence of viscous behavior of the cement line.

Anelastic mechanical response has been observed in all biological materials studied thus far with the possible exception of dental enamel and echinoderm skeletons. Anelastic (or viscoelastic) behavior entails dissipation of energy in dynamic loading, conversion of this energy to other forms, and continued deformation (creep) in response to quasi-static loading. In bone such behavior has been