
ORGANIC ELECTROLYTE LITHIUM BATTERIES

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Dedicated to the 65th anniversary of the late Academician R. Brdička.

Received June 25th, 1970

Interest in organic electrolyte lithium batteries is due, at least in part, to the following advantages, relative to existing commercial batteries: 1. Higher weight energy densities, *i.e.*, in excess of 100 watt h/lb. 2. Longer wet stand shelf life, because of better compatibility of the electrolyte with the plate materials. 3. Discharge capability over a broad range of temperature, *e.g.*, -40° to $+160^{\circ}$ F.

The possibility of achieving these general advantages will be discussed from the point of view of the electrolyte, *i.e.*, its influence on plate stability and discharge rate. The three specific areas considered are: 1. Compatibility of lithium with the electrolyte. 2. Dissolution of the positive. 3. Mass transport within the electrolyte.

Throughout the last decade, there has been a growing interest in the development of batteries employing metallic lithium as the negative electrode. The practical goals of this effort have been low weight batteries, which are capable of long wet stand shelf lives and of operating over a broad temperature range.

Aprotic electrolytes are required for lithium batteries; ionizing organic solvents are one class of material being considered. It is, of course, required that the electrolyte be compatible with both plates and be capable of sustaining reasonable current drains. These electrolyte properties are the subject of the present paper. Emphasis is placed on those specific problem areas which have been critical to the development of practical battery systems.

It will become apparent that many questions regarding the mechanism of electrode and/or electrolyte involvement in overall battery performance are, as yet, unanswered. In this sense then, the present paper is as much an exposition of what remains to be studied as what has been accomplished.

COMPATIBILITY OF ELECTROLYTES WITH LITHIUM

The first major problem in developing a viable lithium-organic electrolyte battery has been the development of electrolytes compatible with metallic lithium. Little distinction is made, at present, between kinetic compatibility and thermodynamic compatibility. Of the many solvents surveyed, the following seem to be sufficiently stable for consideration as the basis of electrolytes: ethylene carbonate, propylene carbonate (PC), butyrolactone (BL), tetrahydrofuran (THF), dimethoxyethane, methylchloroformate, *n*-methylpyrrolidone.

Rigorous calculation of the stability limits of these solvents has not been possible due to the absence of sufficient thermodynamic data. The rigorous experimental determination of stability has been complicated by at least the following: 1. Impurity induced decomposition. 2. formation of protective films on lithium from reaction with the solvent and/or impurities.

One example of these films and their effects is given by the data in ref.¹, a study of the exchange current (I^0) for the reaction

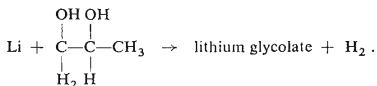


The electrolyte was 0.257 molal LiClO_4 in propylene carbonate; experimental procedures allowed rapid and successive measurements of I^0 after exposure of a fresh lithium surface to the solution. The decrease of I^0 with time is shown in Table I.

TABLE I
Exchange Current for Li/Li^+ as a Function of Time

I^0 , mA/cm ²	>12	10.2	7.8	5.4	2.8	1.6
Time	0	1 s	10 s	1 min	10 min	1 h

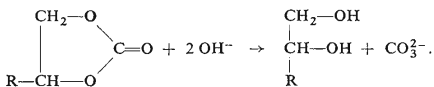
This solution contained less than 0.001 m- H_2O . Deliberate addition of H_2O to bring the concentration to 0.02 m increased the rate of decay of I^0 , *e.g.*, reaching 1.5 mA/cm² after 1 min; further increasing the water concentration to 0.54 m decreased I^0 to ~ 0.1 mA/cm² in 1 min. In the "dry" electrolyte, the double layer capacitance was ~ 45 $\mu\text{F}/\text{cm}^2$, a reasonable value for a rough solid metal surface. In the presence of 0.54 m- H_2O , the capacity dropped to as low as 0.3 $\mu\text{F}/\text{cm}^2$, indicating the formation of a dielectric film on the metallic surface. This is most likely *via*: $\text{Li} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \frac{1}{2} \text{H}_2$, although the following reaction was also possible:



Such films while slowing down the rate of discharge of the lithium electrode, may also provide apparent kinetic stability. For example, we have found that a lithium rod immersed in impure PC gave a small amount of gassing from H_2O which then stopped; the electrode remained metallic in appearance. However, on anodic discharge, gassing resumed from the freshly exposed lithium surface. Presumably a thin film of LiOH protected the surface from rapid reaction.

An example of impurity (electrode and/or electrolyte) induced decomposition is given by the following observations on tetrahydrofuran. If used as received, or after drying, THF will react with lithium thus indicating incompatibility. Yet after distillation and refluxing over metallic lithium, this solvent is rendered sufficiently stable to lead to long shelf life lithium batteries². This decomposition effect has been ascribed to the removal of soluble impurities and surface oxides and/or nitrides from the lithium surface³. According to ref.⁴, THF is also prone to react with dissolved O_2 (and possibly oxides) to form soluble peroxide compounds. Such materials would be sufficiently reactive to directly attack a lithium surface.

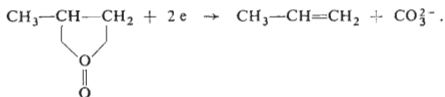
Impurity induced decomposition can, in principal, take the form of acid or base catalysis. It has been established⁵ that cyclic esters, in the presence of aqueous alkali, can undergo the following decomposition reaction:



In the presence of lithium, trace water can provide the required base (LiOH) *via* reaction with lithium. These trace amounts of glycol produced could also react with lithium to form the glycolate, with the evolution of H_2 . As written, the reaction should eventually cease as the OH^- (or H_2O), is consumed. The major significant consequence would be the possible accumulation of carbonate on the lithium surface. The existence of this reaction in "aprotic" solvents has yet to be demonstrated.

Such impurity effects may offer an explanation for the following, apparently contradictory results on the stability of PC-LiClO_4 solutions. In one recent paper⁶ the stability of this electrolyte in the presence of lithium at $+160^\circ\text{F}$ was demonstrated for 900 hours. A second paper reported the evolution of propylene and the formation of carbonate ion from the same electrolyte, at room temperature, on a carbon anode 1 volt positive to Li ,⁷ *i.e.*,





It would be expected that at more negative potentials (*i.e.*, a lithium electrode) this reaction would proceed even more rapidly. In our studies of this phenomenon a carbon electrode was potentiostated at +1.6 V *vs.* Li/Li⁺; eventually visible gassing ceased and the cathodic current decreased to a negligible amount. The potential was then decreased in steps of 0.1–0.2 V in this manner, eventually reaching a value of +0.8 V *vs.* Li/Li⁺. Cathodic current at and above this value, was no longer observed. This suggests catalytic or chemical participation of the carbon electrode in the decomposition process. Since the reaction eventually terminates, the effect does not appear to be entirely catalytic, possibly involving functional groups in the carbon surface.

This reactivity of "inert" electrode surfaces is consistent with the differing cyclic voltammograms run on the same purified solvent but with different electrode materials, *e.g.*, LiClO₄ in PC on Pt and Au. (Fig. 1) At +2.0 to +1.0 V on platinum, water is reduced to H₂. The OH⁻ produced reacts at the electrode surface with lithium ion to form insoluble LiOH, now masking part of the surface. The anodic current at +0.5 V is apparently the formation of Li-Pt alloys.

In large part, therefore, the determination of solvent compatibility becomes an exercise in solvent purification. The ultimate purification of an organic solvent and the inorganic solute is an extensive and time-consuming proposition. Thus, for the practical purposes of developing a battery, an electrolyte will be rejected if apparent

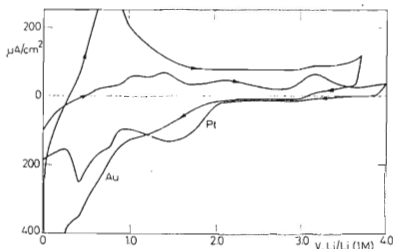


FIG. 1

Background Current Scans on Au and Pt Electrodes in Distilled PC Containing Dried LiClO₄. Scan rate was 74 mV/s; scan was started at +3.7 V.

compatibility is not achieved after employing reasonable purification procedures, adaptable to large scale production. Included under "reasonable purification procedures" are vacuum distillation, deaeration, refluxing over reactive metals, column drying and adsorption. By these techniques we have been able, for example, to reduce total active impurity content of PC to less than $5 \cdot 10^{-4} \text{M-H}_2\text{O}$ and $6 \cdot 10^{-5} \text{M}$ propylene glycol.

DISSOLUTION OF THE POSITIVE

Once a lithium compatible electrolyte has been developed the next hurdle is the selection of a suitable positive plate material. To be suitable in terms of a viable battery, the positive plate material must fulfill the following criteria: 1. Have a low equivalent weight; 2. preferably generate a high electrode potential; 3. be electrochemically stable in the electrolyte; 4. be electrochemically active; 5. be insoluble, *i.e.* $<10^{-5} \text{ mol/l}$; 6. preferably be an electronic conductor.

The most difficult of these criteria to satisfy are items 4 and 5. If the active material is an electronic insulator, an intimate mixture is required with a conductive binder (such as carbon) to provide sufficient points of access for electronic change from the external circuit. Otherwise, the active material must first dissolve so that electroactive ions can reach the conductive positive grid. As will be shown the dissolution mechanism can lead to problems of battery shelf life.

Items 1 and 2 can generally be determined from the literature. Among the materials which have been considered are the following: 1. The elements, *e.g.*, O_2 , S, Br_2 , I_2 ; 2. transition metal oxides, *e.g.*, MnO_2 , PbO_2 , Ag_2O ; 3. transition metal fluorides, *e.g.*, NiF_2 , CuF_2 ; 4. transition metal chlorides, *e.g.*, NiCl_2 , CuCl_2 , AgCl ; 5. transition metal sulfides, *e.g.*, Ni_3S_2 , CuS .

Calculated thermodynamic cell potentials and the maximum energy densities (*i.e.*, considering only the weights of the active materials) are listed in Table II. To put this data into context, the thermodynamic cell potential for the $\text{Zn}(\text{KOH}, \text{H}_2\text{O})\text{AgO}$ battery is 1.71 V; the maximum energy density is 254 watt h/lb. Obviously then, many of the couples listed have the potentiality of yielding energy densities substantially higher than achievable with aqueous systems.

The problem of electrochemical stability (criteria 3) does not appear to be significant with the solvents mentioned at the beginning; most of those can be taken to +3.5–4.0 V (*vs.* Li/Li^+) before solvent decomposition is observed.

Most of the positive electrode compounds mentioned above are electrochemically active. Discharge mechanisms have not been explored in any great detail; a few pertinent facts are known, however. For example⁸ oxygen in PC and DMSO discharges at useable potentials as follows:

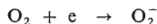


TABLE II
Characteristics of Lithium Battery Couples

Positive	Cell potential V	Maximum energy density Wh/lb
O ₂	2.9	2 794
S	2.6	1 350
Br ₂	3.53	584
MnO ₂	1.7	981
NiF ₂	2.83	620
CuF ₂	3.55	754
CuCl ₂	3.06	505
AgCl	2.84	231
CuS	2.15	563
Ni ₃ S ₂	1.8	388

rather than



Thus, only one electron rather than four is involved in the discharge, yielding an equivalent weight (per O₂) of 32 rather than 8. If a small amount of water was present O₂ reduction proceeded to yield OH⁻ (ref.⁹):

Sulfur apparently discharges to form soluble polysulfides such as S₈²⁻ rather than S²⁻ (ref.¹⁰). This leads to a lower equivalent weight and the possibility of chemically short circuiting the lithium electrode with soluble electroactive material.

Bromine is slightly soluble and discharges readily to bromide ion. However, in some solvents, *e.g.*, PC, Br⁻ will react with Br₂ to form soluble Br₃⁻. A similar solubilization phenomenon has been reported for the CuCl electrode in propylene carbonate electrolytes (see below).

A number of the transition metal compounds must apparently dissolve before discharging. This seems to be the case for PbO₂ and Ag₂O; our preliminary studies indicate that the discharge of CuF₂ in PC is also preceded by dissolution.

The fate of soluble positive plate material containing transition metal ions is usually the deposition of base metal on the more electropositive negative plate. This consumes active material from both plates, but more important, leads to dendrite growth of the base metal which eventually bridges the electrolyte space, shorting the cell.

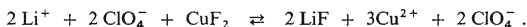
The pertinent solubility variables for battery construction are the following: 1. The net solubility; 2. the rate of dissolution; 3. the fate of the soluble positive plate material.

Some semiquantitative data is available for total solubility; very little information is available on dissolution rates, although it has been reported¹¹ that solubility is proportional to the rate of dissolution. The selection of positive materials which are both electrochemically active and insoluble has been the major problem area with positive electrodes. For practical purposes, the total solubility should be substantially less than $4 \cdot 10^{-4}$ mol/l. This is the solubility of silver oxide in aqueous KOH (7M) for which an extensive separator system is required to prevent deposition of metallic silver on the negative.

Three general solubility mechanisms have been observed: 1 Direct dissociation of the compound; 2. metathetical decomposition reactions with the solute; 3. complex ion formation with discharge product.

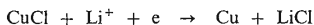
The first of the solubility mechanisms mentioned requires little comment, referring to reactions of the type $\text{CuS} \rightleftharpoons \text{Cu}^{2+} + \text{S}^{2-}$.

Mechanism (2) is best illustrated by the following equation:



Presumably, because of the greater insolubility of LiF, the reaction proceeds to the right. Unfortunately there is insufficient data on the solubility of $\text{Cu}(\text{ClO}_4)_2$ to permit a thermodynamic calculation of the equilibrium constant for the above reaction. It has been observed^{12,13}, however, that the effective solubility of CuF_2 is higher in solutions containing LiClO_4 than in the solvent itself (Table III). Note also that small amounts of water (in the as received solute) also increase the amount of soluble CuF_2 .

The third solubility mechanism is best illustrated by the behavior of CuCl in a LiAlCl_4 -PC electrolyte. A freshly prepared electrode has a solubility of $4.6 \cdot 10^{-3}$ mol/l (ref.¹⁴). On discharge, *i.e.*,

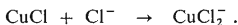


some soluble chloride is formed, equal to the solubility of LiCl ($\sim 10^{-2}$ mol/l in PC).

TABLE III
Solubility of CuF_2 in PC Solutions

Solution	Solubility	
	mg Cu^{2+} /l	mol CuF_2 /l
solvent	12	$1.9 \cdot 10^{-4}$
solvent + LiClO_4 (as received)	260-385	$4.1-6.1 \cdot 10^{-3}$
solvent + LiClO_4 (purified)	34-56	$6.1-8.8 \cdot 10^{-4}$

This chloride ion can now react with CuCl as follows:



The soluble electroactive copper chloride complex ion is now free to self discharge at the lithium negative. The same solubility mechanism applies to the AgCl electrode.

Apparently, there is at least one electrolyte system in which this complex ion reaction does not take place, methylchloroformate containing LiAlCl_4 as solute². However, the solubility *via* the first reaction is apparently high enough to render this system impractical as a long wet stand shelf life battery.

Thus, the transition metal halides have problems with excessive solubility; many oxides which are electrochemically active seem to be soluble; there are problems in using the elements (*e.g.*, S, O₂, Br₂) due to incomplete reactions, excessive solubility and/or packing. A number of workers^{2,15} have considered the use of transition metal sulfides in an attempt to circumvent these difficulties. At least two member of this class of positive material, Ni₃S₂ and CuS, are sufficiently insoluble and yet electroactive to result in the development of prototype batteries. These sulfides have a higher equivalent weight than the oxides and some of the halides, as well as a lower potential *vs.* a lithium electrode. Nevertheless, batteries with energy densities in excess of 100 watt hour/lb have been built. Both of these sulfides have been reported to be electronic conductors, which fact may have an important implication on their discharge mechanism. The discharge mechanisms of both materials have yet to be reported. It is to be expected, however, that it should not be necessary for these compounds first to dissolve in order for electroactive material to reach the conducting positive grid, *i.e.*, the electron source. Since solubility is low, then the rate of dissolution¹¹ should also be low and thus the self-discharge rate should be low. Indeed long wetstand shelf lives have been demonstrated for the Li/CuS system².

ELECTROLYTE MASS TRANSPORT

The stability and solubility considerations discussed above, in essence, determine whether a stable lithium-organic electrolyte battery is at all feasible. The practical applications of such batteries, once feasibility has been demonstrated depend upon the current drains possible with minimal cell polarization. The ultimate drain rate is determined by the current carrying capabilities of the electrolyte.

The initial surveys considered principally solvents with high bulk dielectric constants. It has subsequently been shown that a low dielectric constant is not necessarily a valid criterion for rejecting a solvent. For example, THF, with a dielectric constant of 7.4 is as good, if not better, an ionizing solvent for Li salts than propylene carbonate which has a dielectric constant of 67.

A better survey parameter is the specific conductance. A high conductivity is obviously desirable. However, in most prototype battery systems the drain rate capabilities are not limited by ion conductivity. For example, an electrolyte such $1M\text{-LiClO}_4$ in propylene carbonate with a conductivity of approximately $5 \cdot 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$, would sustain across a 10 mil gap (0.254 mm) 40 mA/cm^2 with an 0.2 V loss. Severe cell polarization is generally experienced before this current density is reached.

Ion current limitations in terms of the mobility of soluble charge carriers have been considered in reference¹⁶. The conditions for calculations were a AgNO_3 solution between silver anode and cathode. Analogous to this is a $\text{LiClO}_4\text{-PC}$ solution between a lithium anode and an electroactive cathode consuming lithium ion to yield an insoluble lithium salt, *e.g.*, LiF or Li_2S . We will consider only the concentration overpotential at the cathode. The equation developed to describe the limiting current density is:

$$i_1 = \frac{D_1 F z_1 C_0}{d} \left(1 + \frac{z_1}{z_2} \right),$$

where D_1 is the diffusion coefficient of the discharging ion, d is the electrode separation and C_0 is the concentration of ions at the anode; C at the cathode is assumed to be zero, *i.e.*, each Li^+ ion to arrive is consumed. In effect a linear concentration gradient is assumed. Thus, in terms of the original composition of the electrolyte (C^1), the following identity should hold, $C_0 = 2C^1$. Taking this into consideration and assuming a diffusion coefficient of $6 \cdot 10^{-7} \text{ cm}^2/\text{s}$ (ref.¹⁷), i_1 for the case above computes as 8 mA/cm^2 .

The critical factor in these calculations is the diffusion coefficient; very little data is available for the solvents of interest, (*e.g.*^{17,18}). Diffusion coefficients have been related to ionic mobilities *via* the Nernst-Einstein equation¹⁹:

$$u = D/FC = DF/RT$$

and thus

$$D_1 + D_2 = A = (F^2/RT)(D_1 + D_2).$$

Thus, to the extent that this relationship is obeyed, conductance is a valid indicator of diffusion coefficient. This relationship has been questioned, however, for concentrated aqueous salt solutions^{19,20}.

A more valid screening technique, involving directly the diffusion coefficient is a transition time - chronopotentiometric method¹⁷ employing the reaction $\text{Li} \rightarrow \text{Li}^+ + e$. A lithium cathode is subjected to a constant current and the transition time measured. The longer the transition time, the larger is the diffusion coefficient. Unfortunately, long transition times are difficult to measure accurately. Such a technique still does not answer the questions: 1. what electrolyte systems should be eva-

luated based on published data, and 2. how could electrolytes be modified to increase their current carrying properties?

Although there is little data available on diffusion coefficients, there is more information on viscosities². To a first approximation

$$D = \text{constant}/\gamma,$$

where γ is viscosity. Thus, Levich's limiting current equation for a given solute type becomes

$$i_l = KC^0/\gamma,$$

where

$$K = \frac{k^1 F z_1}{d} \left(1 + \frac{z_1}{z_2} \right).$$

According to the literature¹⁸, the relationship between D and γ is constant within $\pm 16\%$ for a variety of organic solvent-electrolytes, if the viscosity of the bulk solvent is used; the consistency is significantly poorer if the viscosity of the solution is used.

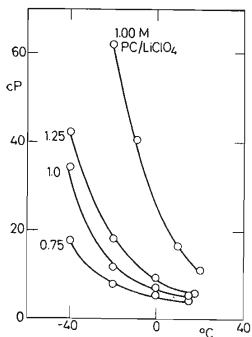


FIG. 2

Viscosity-Temperature Relationships for Solution of LiClO_4 in PC and BL

Upper curve PC/ LiClO_4 ; three remaining curves BL/ LiClO_4 .

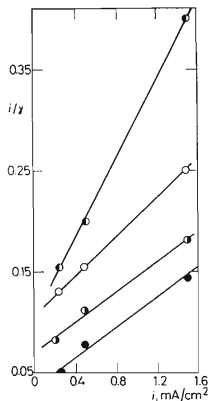


FIG. 3

Current Density-(Viscosity)⁻¹ Relationships for $\text{Li}/\text{Ni}_3\text{S}_2$ Cells at Constant Potentials (● at 1.5 V; ○ at 1.4 V; ● at 1.24 V); in 1M- LiClO_4 -BL electrolytes.

Qualitatively at least, the limiting current and any current i_1 in a given electrolyte system should be inversely proportional to the viscosity. In Fig. 2 is shown the viscosity-temperature profile for LiClO_4 in PC and in butyrolactone. The temperature dependence of potential for laboratory $\text{Li}/\text{Ni}_3\text{S}_2$ cells discharged in these electrolytes at $0.25 \text{ mA}/\text{cm}^2$ to 20% depth of discharge has been reported previously²¹. Cross plotting these data in terms of $1/\eta$ vs. i (at constant potential) yields the curves in Fig. 3. Obviously, these are in at least qualitative agreement with the current relationship described above.

It would be expected that diluting high viscosity solvents with low viscosity solvents would yield systems of improved discharge performance and intermediate physical properties. This has been observed for mixtures of PC and BL with THF. A summary of these results is given in ref.²².

REFERENCES

1. Butler J., Cogley D., Synnott J.: *J. Phys. Chem.* 73, 4026 (1969).
2. Gabano J. P., Gerbier G., Laurent J.: *Proceed. 23 Annual Power Sources Conf. Atlantic City, New Jersey* 1969.
3. Gabano J.: Personal communication.
4. Mann C. K.: *Electroanalytical Chemistry* (A. Bard, Ed.) p. 98, Vol 3. Dekker, New York 1969.
5. Saadi A., Lee J.: *Chem. Soc.* 1968, 1.
6. Jasinski R., Carroll S.: *J. Electrochem. Soc.* 117, 218 (1970).
7. Day A., Sullivan B.: *J. Electrochem. Soc.* 117, 222 (1970).
8. Jasinski R., Kirkland S.: *Anal. Chem.* 39, 1663 (1967).
9. Toni J., Waagstra: *Final Rept. Contract DA 44-009-AMC-1552(T)*, July (1967).
10. Merritt M., Sawyer D.: *Inorg. Chem.* 9, 211 (1970).
11. Vermilyea D.: *J. Electrochem. Soc.* 113, 1067 (1966).
12. Boden D., Buhner H., Spera V.: *Final Rept. Contract DA 28-043-AMC-01394(E)* (AD639709), September (1966).
13. Boden D., Buhner H., Spera V.: *Final Rept. Contract DAA 1307-67-C0385* (AD67867), October (1968).
14. Rao M. L. B.: *J. Electrochem. Soc.* 114, 13 (1967).
15. Jasinski R.: *Ref.* 14, 166, 422 (1969).
16. Levich V.: *Physicochemical Hydrodynamics*, p. 247. Prentice Hall, New York 1962.
17. Gabano J. P., Jumel Y., Laurent J.: *Power Sources* 12, (D. Collins, Ed.). Pergamon Press, London 1970.
18. Sullivan J., Hanson D., Keller B.: *J. Electrochem. Soc.* 117, 779 (1970).
19. Robinson R., Stokes R.: *Electrolytic Solutions*. Butterworths, London 1959.
20. Hartley G.: *Phil. Mag.* 12, 473 (1931).
21. Jasinski R., Gaines L.: *Proceed. 24 Annual Power Symp. Atlantic City, New Jersey, May* 1970.
22. Jasinski R.: *Advances in Electrochemistry* (C. Tobias, Ed.), chapter 4. Wiley, New York 1970.