

THE REACTIVITY OF ORGANIC ELECTROLYTES WITH LITHIUM: MECHANISTIC ASPECTS

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Summary

The overall rate of Li-organic electrolyte reactivity is governed by heterogeneous redox chemistry at the Li electrode surface and by homogeneous acid-base chemistry in the bulk. While the former mode of reactivity may lead to protective films, the latter mode invariably results in rapid electrolyte degradation with time and must be considered the most serious source of poor cycling life in rechargeable cells.

1. Introduction

Over the past five years, the kinetic stability of organic electrolytes to the secondary Li electrode has been markedly improved [1]. Prototype ambient temperature rechargeable cells incorporating transition metal chalcogenides [2] and transition metal oxides [3] have undergone in excess of two hundred deep cycles. Yet the chemical and electrochemical factors leading to a "stable" electrolyte are not well understood. Further advances in Li electrode cycleability are contingent upon obtaining an appreciation of which modes of reactivity can and cannot be tolerated.

On the basis of research to date, it appears that there are three major factors which influence the rate of Li-electrolyte reactivity:

- The kinds and concentrations of reactive impurities.
- The anion of the supporting electrolyte.
- The stereo-electronic properties of the solvent molecule itself.

Electrolyte contaminants, certain anions, and the solvent are known to react in the bulk solution as well as on the Li surface [1]. The relative importance of homogeneous and heterogeneous reactivity is crucial in designing an organic electrolyte for secondary Li systems.

2. Reactive impurities

A variety of techniques have evolved which remove or, at the very least, substantially reduce the concentration of reactive impurities in the electro-

lyte. Thus, the use of surface active materials such as alumina [4], distillation of solvent off getters such as benzophenone ketyl [5] or lithium naphthalide [6], solvent reflux over NaK or Li-Hg amalgam [7], and pre-electrolysis between two Li electrodes [8] have helped remove reactive gases and protic contaminants. In one documented case, however, stringent purification of 2-methyltetrahydrofuran (2-Me-THF) failed to remove several aprotic contaminants: tetrahydrofuran (THF), tetrahydropyran, and methylfuran [10].

Remaining traces of protic impurities dissolved in an electrolyte ought not to affect Li electrode cycling behavior seriously. This is because these impurities are rapidly and irreversibly scavenged by Li to give insoluble (immobilized) reaction products, *e.g.*, N_2 to Li_3N ; H_2O to $LiOH$; CO_2 to Li_2CO_3 . Real damage to an electrolyte is caused by a soluble impurity which reacts with either anion or solvent and then, in some cases, is regenerated at the Li surface.

3. Degradation chemistry of the anion

An examination of anion stability in Li secondary cells reveals that degradation chemistry may proceed both heterogeneously (at the anode or cathode) and homogeneously. In the former case, AsF_6^- was found to be reduced by Li to AsF_3 [8] (eqn. (1)).

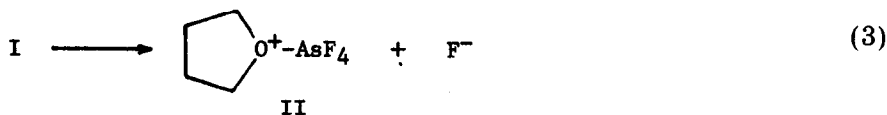
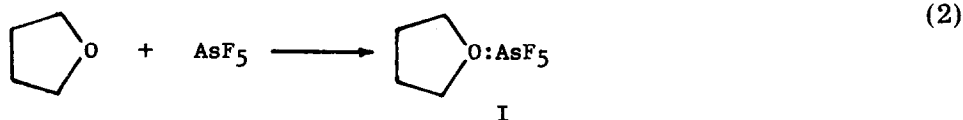


More recently, some organoborates were observed to oxidize at a charged TiS_2 cathode [11], and Cl^- from ClO_4^- was found on the Li surface by ESCA techniques [12].

Although AsF_6^- reduction in ethers forms what appears to be a beneficial "brown film" on the Li surface [9], long term cycling invariably consumes the anion, resulting in increased cell impedance.

The homogeneous reactivity of anions in the absence of Li ranges from shock sensitive $LiClO_4/1,3$ -dioxolane solutions [13] to the slow, room temperature degradation [14] and rapid, thermally induced decomposition [15] of $LiAsF_6$ /ether electrolytes. In both cases it appears that traces of AsF_5 react with an ether such as THF to form a thermally unstable oxonium ion (II) (eqns. (2), (3)).

The oxonium



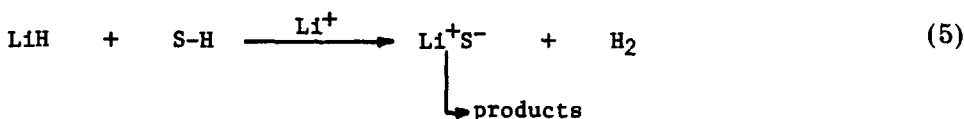
The oxonium ion then decomposes to give alkyl fluorides and arsenic oxyfluorides along with the polymerization of THF. As long as there is a source of AsF_5 , this process continues. Fortunately, this degradation process is arrested by the presence of Li, which presumably scavenges AsF_5 .

4. Degradation chemistry of the solvent

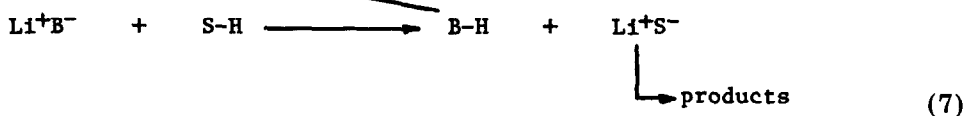
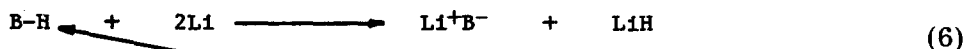
Recent evidence suggests that the kinetic stability of an organic solvent toward Li is influenced by the relative position of its lowest unfilled molecular orbital [16]. Thus, α -methylated tetrahydrofurans and pyrans are more difficult to reduce than their non-alkylated homologues. In addition to this electronic effect, steric effects are also operative. When a 50:50 mixture of *cis/trans* 2,5-dimethyltetrahydrofuran was fractionated to give 80:20 mixtures of each isomer, the *cis*-enriched fraction was found to be more stable to Li than the *trans*-enriched fraction [17]. These particular stereo-electronic effects are interpreted as arising from the propensity (or lack thereof) of an ether to heterogeneously reduce on a Li surface (eqn. (4)).



A second heterogeneous route to solvent degradation has recently been reported, *i.e.*, LiH metallation in the presence of Li^+ [18]. When 1,3-dioxolane was stored with LiH and a soluble Li^+ salt at 80 °C, the LiH metallated the solvent at carbon atoms bearing acidic hydrogen (eqn. (5)).

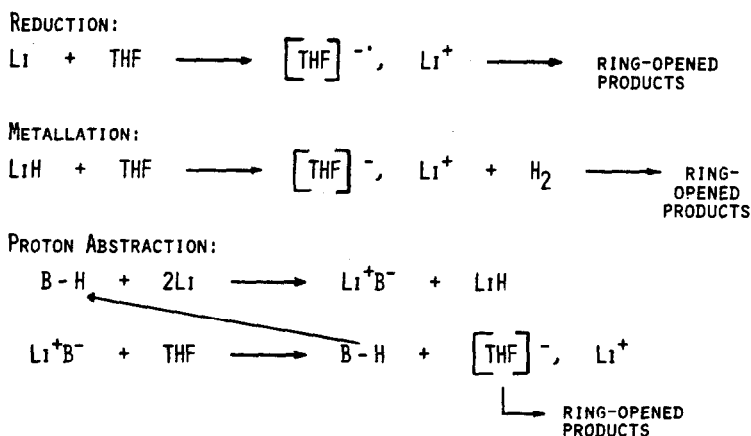


By analogy with LiH metallation, the most damaging reaction a solvent can undergo is proton abstraction in the bulk. An organic contaminant with a labile hydrogen (B-H) may react at the Li surface, forming a soluble carbanion (B^-). This carbanion is sufficiently basic so as to abstract a proton from a solvent molecule in the bulk. A shuttle mechanism sets up whereby the re-protonated carbanion again reacts at the Li surface according to eqns. (6) - (7).



The organic contaminant may be turned over many times, generating an equivalent of LiH with each turnover. Possible candidates for B-H include allylic or longer chain conjugated unsaturated species possessing a labile hydrogen.

The worst possible case for solvent decomposition involves three competing reactions shown in Scheme 1. Using THF as an example, direct reduction by Li, metallation by LiH, and proton abstraction by B⁻ all lead to the same kinds of ring-opened products.



Scheme 1. Competing heterogeneous and homogeneous solvent reactions.

5. Conclusion

While electrolyte purification is a necessary requirement for good cycling efficiencies, it is by no means sufficient. Sub-ppm traces of certain impurities can cause extensive solvent decomposition. Moreover, it has been suggested that one consequence of heterogeneous solvent reduction by Li is the generation of a strong soluble base which, in turn, reacts with solvent in the bulk [8]. Because Li-electrolyte reaction products are thermodynamically more stable than the reactants, the best that one can do is to minimize adventitious impurities while choosing solvents resistant to reduction by Li and proton abstraction by strong bases.

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