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STATUS OF THE SECONDARY LITHIUM ELECTRODE

V. R. KOCH*

EIC Laboratories, Inc., 55 Chapel Street, Newton, MA 02158 (U.S.A.)

Summary

Over the past decade, several major advances have been made in improving the cycling efficiency of the secondary Li electrode. This review article summarizes the research leading up to these advances and describes "state-of-the-art" electrolytes for normal temperature, secondary Li batteries, as reported in the open literature. Remaining problems are identified and areas for additional research are suggested.

1. Introduction

Since the thesis work of Harris [1], the prospect of a normal temperature, high energy density, rechargeable Li battery has stimulated an international research effort. Although prototype cells have been fabricated by Bell Laboratories, EIC Laboratories, and Exxon Enterprises, Inc., only one rechargeable Li battery (a $LiAl/TiS_2$ button cell) has, to date, been commercialized. This cell, manufactured by the Battery Division of Exxon Enterprises, had limited capabilities [2] and was subsequently withdrawn from the market in late 1979.

The principal reason for the slow evolution of this technology resides in the inability to cycle the Li electrode at high capacities with high efficiency over a long period of time. Accordingly, this review summarizes the work accomplished during the past decade and suggests some fruitful areas for further research. Indeed, most of the progress in improving the cyclability of the secondary Li electrode has been realized within the last 4 years. Earlier efforts have been adequately reviewed by Jasinski [3, 4], and, more recently, by Besenhard and Eichinger [5].

2. The problem

It is known that Li may be plated onto a conducting substrate from a variety of aprotic organic electrolytes with 100% efficiency [6 - 8]. Subsequent anodic dissolution, however, is invariably less efficient [6 - 10]. The

*Present address: Covalent Associates, Framingham, Massachusetts 01701 (U.S.A.).
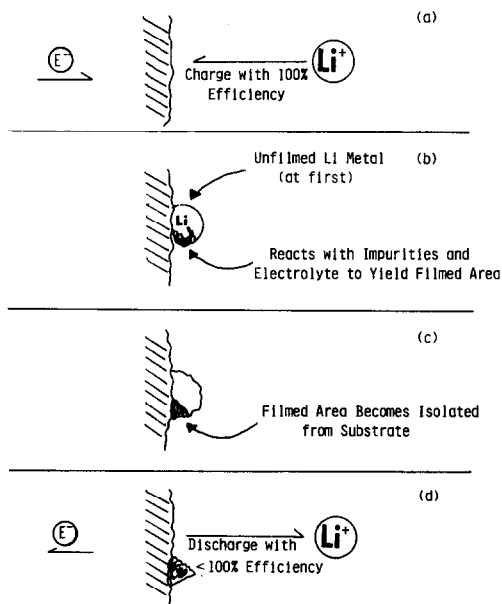
Fig. 1. Scenario illustrating the source of secondary Li electrode inefficiency [9].

difference reflects Li metal electrically isolated from the substrate by passivating, albeit Li^+-conducting films [9, 11 - 13]. These films arise from the reduction of reactive impurities and the electrolyte itself, thus protecting the underlying Li from further dissolution [14, 15]. Although this process confers stability to the Li electrode in a number of primary cells [11], the consequences of film formation have been disastrous for a rechargeable Li electrode.

Consider a likely scenario (Fig. 1): Li is deposited with 100% Faradaic efficiency; the freshly nucleated Li reacts with electrolyte impurities (H_2O, protic organics, dissolved gases such as N_2, O_2, CO_2) at a high rate, then with solvent and salt at a lower rate; the Li becomes electrically isolated from the conducting substrate either through the formation of insulating films or by Li erosion at the substrate–Li interface [8]; on discharge, less than 100% of the initial charge is electrostripped (cycling efficiency = charge stripped/charge plated). The residual dendritic Li results in an irregular surface which seriously distorts the morphology of subsequent plates. On the second plate, for example, Li nucleation and growth proceed irregularly, forming additional dendrites. The surface area of the plate correspondingly increases and the overall rates of reaction with impurities and electrolyte increase, and more Li is isolated. Thus, the effect of a small morphological perturbation of the first cycle becomes compounded over several cycles, leading to a cascading loss of efficiency and ultimate electrode failure.

More recently, Peled has interpreted the poor stripping efficiencies of alkali and alkaline earth metals in terms of a solid electrolyte interphase
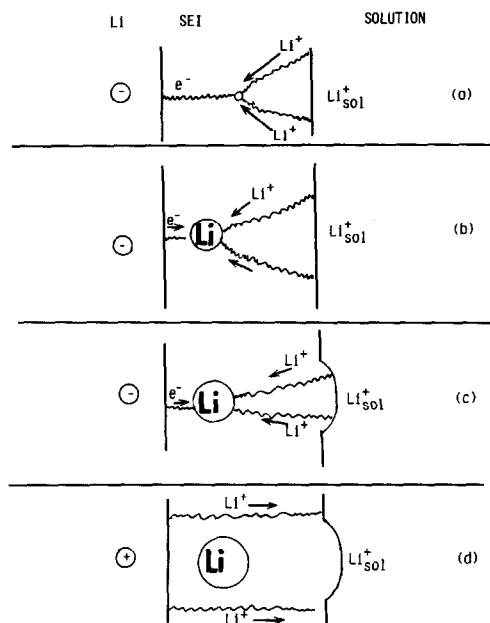
Fig. 2. The effect of a partial short on the deposition–dissolution process for the SEI model [16].

(SEI) model (Fig. 2) [16]. The SEI comprises a Li^+-conducting film. High plating current densities and/or a poorly conductive interphase result in the formation of a short circuit through the SEI on charge (Fig. 2(a)). Thus, a parcel of Li metal forms within the SEI, out of direct electrical contact with the substrate. The short circuit disappears after plating ceases, and, on subsequent discharge, the encapsulated parcel of Li is unavailable for electro-dissolution (Fig. 2(d)).

    While the intimate chemical and electrochemical details of the Li isolation process are open to speculation, a wide variety of innovative strategies have been developed in an attempt to cope with this problem.

3. Strategies to improve the cyclability of the Li electrode in aprotic organic media

3.1. Electrolyte purification

    There is universal agreement that protic impurities (particularly H_2O) react rapidly with freshly plated Li. Accordingly, this reaction may mask the intrinsic reactivity of the solvent itself with Li. Indeed, this has been demonstrated in recent work with propylene carbonate (PC) [14] and tetrahydrofuran (THF) [15].

    A 1M $LiClO_4$/PC electrolyte was purified by first passing the solvent through activated alumina, and then by pre-electrolyzing the solution

formed by LiClO$_4$ addition [14]. The pre-electrolysis procedure involved the galvanostatic deposition of Li onto a Ni cathode. Thus, any protic impurity introduced by the LiClO$_4$ would be scavenged at the freshly deposited Li surface. The use of alumina and pre-electrolysis afforded high efficiency values for the first few cycles. However, a precipitous loss in efficiency was found on subsequent cycling [14]. This behavior was interpreted in terms of the slowly forming Li–PC reaction products being ultimately more damaging to Li morphology than were the rapidly formed Li–protic reaction products.

More recently, THF, distilled off benzophenone ketyl and sealed with Li in a Pyrex ampoule under Ar, was found to react more rapidly with Li than THF contaminated with H$_2$O and reactive gases [15]. Since earlier work with PC [9] and THF [10] revealed that the deliberate addition of small amounts of H$_2$O and reactive gases improved cycling efficiencies, it is clear that PC and THF are intrinsically reactive towards Li. Increases in "stability" of PC and THF with Li are most likely due to solvent-impermeable films, as has been pointed out by Jasinski [17]. Indeed, a recent thermodynamic analysis of the direct interaction of Li with a variety of aprotic organic solvents demonstrated that all may, in principle, be reduced by Li [18].

Although the use of alumina [19] and benzophenone ketyl [20] has found favor in electrolyte purification schemes, it is clear that stringent purification procedures alone are, for some solvents, actually inimicable to achieving good Li cycling efficiencies.

3.2. Li surface active additives

Since all organic media would appear to be thermodynamically unstable with respect to Li, and since Li–electrolyte/Li–impurity reaction products lead to films, a considerable amount of effort has been directed at modifying the Li surface so as to form beneficial Li$^+$-conducting films. Another approach is to improve the Li morphology on plating through the agency of leveling agents. Phenomenologically, one cannot say where good morphology ends and a conductive film begins, or *vice versa*. What has been established is that small concentrations of additives dramatically affect Li cycling efficiencies.

Broadhead and Trumbore reported that tetraglyme, a polyether, improved the morphology of Li electrodeposited from a Bu$_4$NCl, LiClO$_4$/PC electrolyte [21]. The better morphology may be due to the polyether's ability to wet the substrate surface, thereby allowing a less energetic Li nucleation process to occur on charge.

Besenhard noted that the use of LiI as a supporting electrolyte in PC afforded better Li cycling behavior [22]. Conceivably, the presence of I$^-$ in the SEI [16] improves Li$^+$ conductivity through the film and, thereby, Li plate morphology.

An extensive investigation into film-forming "precursors" (surface-active additives) was recently completed at EIC Laboratories in PC, THF, and methyl acetate (MA) media [9, 23, 24]. Precursors (generally at 0.1M)

were chosen from those which were likely to form passivating films on Li. The rationale for the choices is given in ref. 23 (p. 54, *et seq.*). The compounds investigated as precursors were: CS_2, $PSCl_3$, $POBr_3$, $PNBr_2$, $POCl_3$, $MoOCl_4$, CH_3NO_2, $VOCl_2$, CO_2, N_2O, and SO_2. The cycling regime was $i_p = i_s = 2.5$ mA/cm^2; $Q_p = Q_s = 10$ C/cm^2 (p = plating; s = stripping). Baseline efficiencies for Li on Li cycling in 1M $LiClO_4$/PC averaged 40%. Several precursors ($POBr_3$, N_2O, SO_2), individually added to the electrolyte, increased the efficiency to the 70 - 85% range while others (CO_2, $POCl_3$, CH_3NO_2) afforded less than 40% efficiency [23]. The mode of operation of these compounds and the nature of the interphase is presently unknown.

Metal cation additives which co-deposit with Li$^+$ to form non-dendritic, Li-rich intermetallics or alloys are the subject of a recent patent [25]. Thus, salts such as $CaBr_2$, $ZnBr_2$, or $HgCl_2$ in 0.25M concentration with $LiClO_4$/PC or acetonitrile saturated with SO_2, comprise this electrolyte.

Work at EIC with cyclic ether solvents and $LiAsF_6$ has shown that the AsF_6^- anion itself may function as an additive [15]. Thus, AsF_6^- was found to reduce on a fresh Li surface to AsF_3. The AsF_3 in turn reacted with Li alkoxides (products from solvent reduction by Li) to form a "brown film". This film appears to be composed of a polymeric material having a $(-As-O-As-)_n$ structure [15]. Whether this film improves cycling effi-

ciencies by interposing itself between Li and the reactive electrolyte, or by scavenging deleterious Li-solvent reaction products, is open to question.

3.3. Use of alloying substrates

Dey reported that Li alloys spontaneously and/or forms intermetallic compounds with a variety of metals and semiconductors, among them Ag, Al, Au, Cd, Mg, Pd, Pt, Sn, Zn, and Si [26]. Alloy formation can be used to protect Li from attack by an aggressive electrolyte environment in two different ways: Li may be sequestered within a metallic host thereby preventing physical contact between Li and the electrolyte; Li-metal alloys manifest a potential positive to that of pure Li, thereby lessening the thermodynamic driving force for Li—electrolyte reaction at the interface.

Various research groups have worked on this approach, Al being the most popular alloying substrate [8, 23, 27 - 33]. The consensus is that while the alloy does afford initially high efficiencies, subsequent cycling invariably causes severe roughening and ultimate disintegration of the electrodes. During this process, particles of Li—Al and Al lose contact with each other and the electrode structure crumbles. Van Beek and Rommers conclude that "it is questionable whether alloying substrates will find practical application in rechargeable Li batteries because of the decrease in energy density and the disintegration processes on cycling" [8].

3.4. Internally generated Li scavengers

As mentioned earlier, the inability to strip all electrodeposited Li ultimately leads to electrode failure. If encapsulated Li metal could be returned

to the electrolyte as Li^+, the dendrite problem would be obviated and the active Li mass conserved. The implementation of this concept requires that a material be added to the electrolyte which is normally inert, *e.g.*, LiBr, but which may be converted into a scavenger (Br_2) which will subsequently oxidize Li to Li^+. The scavenger redox potential must be above the potential of the positive electrode. Hence, the reduced scavenger (Br^-) will be present in the normal (non-corrosive) form. Accordingly, the self-discharge rate on stand will be very low. With a positive-limited battery, the scavenger could be generated on overcharge or on an auxiliary electrode. A better alternative would be to employ a negative-limited configuration, and to overdischarge the system. This would generate the scavenger (*e.g.*, Br_2) right at the Li-electrode substrate. This scavenger would attack and redissolve the encapsulated Li. Since there would be no other Li metal available, good efficiency would be anticipated.

There is evidence from the literature [34, 35] that this is a viable approach: Weininger *et al.*, explored the Li/Br_2 cell and achieved ~ 1800, ~ 3 C/cm^2 charges and discharges. This is by far the largest number of cycles that has been reported for Li in organic electrolytes. The most likely reason is that the dissolved Br_2 positive kept the Li-electrode substrate free from encapsulated Li.

Criteria for selection of scavengers are:

(i) They (and where there are Li^+ salts of their reduction products) must be soluble.

(ii) The scavenger redox potential must be above the potential of the positive electrode.

(iii) The scavenger redox process must be simple.

Preliminary investigations of this concept in MA (Br^-/Br_2) and THF (I^- and S^{2-}/S_n^{2-}), have been carried out at EIC with some interesting results [23].

3.5. The "recontacting" phenomenon

Work with 1M $LiAsF_6$/THF electrolyte revealed that dendritic (isolated) Li on a Ni substrate could, on occasion, be electrochemically recouped [10]. A freshly plated charge of Li stored on open circuit for 16 h invariably gave a poor stripping efficiency due to Li self-discharge (encapsulation). However, subsequent plating and stripping allowed the recovery of a portion of the Li isolated during the 16 h storage. Specifically, the isolated Li was recovered on the strip immediately following the first post-storage plate. The operative mechanism is unclear, although the dissolution of insulating films (Fig. 1), or a reorganization of the SEI (Fig. 2) with time are possible explanations. Clearly, if one could chemically or electrochemically control recontacting, Li conservation would be dramatically increased.

3.6. Structural modification of the solvent molecule

As mentioned earlier, stringently purified PC and THF were found to be highly reactive toward Li [14, 15]. Selim and Bro have pointed out that

organic molecules possessing a dipole may well be intrinsically reactive toward Li [6]. By inference, all aprotic organic solvents suitable for Li battery electrolytes are thermodynamically unstable with Li, as has been determined by Kedrinskii and co-workers [18]. Given an aprotic organic electrolyte, one can only hope to stave off the inevitable by retarding reaction kinetics. Film-forming additives and alloying substrates are two methods of affecting the kinetics. Another approach is to slow Li–solvent reactivity by altering the structural features of the solvent molecule itself. This has been demonstrated by Koch and co-workers who replaced THF by 2-methyltetrahydrofuran (2-Me-THF) [36 - 38].

The reduction of ethers by alkali metals is postulated to involve a one-electron transfer from Li to the lowest unfilled molecular orbital (LUMO) centered on the ether's oxygen atom [15]. If, in fact, this is the rate-determining step for ether reduction, one could then raise the activation energy of that step by perturbing the energy of the LUMO upward. An electron-donating substituent of a carbon atom adjacent to the ether's oxygen atom would accomplish this. Thus, Koch found that 2-Me-THF (I) was highly resistant to reduction by Li, while 3-methyltetrahydrofuran (3-Me-THF) (II), a positional isomer of 2-Me-THF, was as reactive as THF towards Li [38]. The inductive effect of a 3-methyl substituent does not perturb the LUMO and 3-Me-THF is therefore readily reduced by Li.

I   II
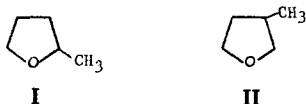
4. Aprotic organic electrolyte systems commonly used in secondary Li research

Having considered several strategies to improve the cycling efficiency of the Li electrode, it is appropriate to review the commonly used solvent/salt combinations employed over the past decade of research. In this regard, a comprehensive list of useful classes of organic solvents for Li batteries has been assembled by Kronenberg in a recent patent [39].

Without question, the $LiClO_4$/PC electrolyte has been the most studied medium in which to cycle the Li electrode. Because of the formation of an insoluble Li_2CO_3 surface film, purified PC manifests excellent stability when stored with Li at elevated temperatures [4]. More recently, the Groupe de Recherche no 4 du CNRS has, in a series of publications, investigated PC/Li reaction kinetics in concert with X-ray analysis and scanning electron microscope (s.e.m.) studies [33, 40 - 44]. They find that low current densities during cycling are necessary in order to preserve the integrity of the passivating film, thereby minimizing dendrite formation. In addition, they report a significant LiCl concentration along with Li_2CO_3 among the prod-

ucts in the passivation layer [33]. This is the first published report of the ClO_4^- anion's reactivity in a PC-based medium.

Li cycling efficiencies on a Li substrate have been determined in $LiClO_4$/PC and $LiAsF_6$/PC media [45]. It was found that for 10 C/cm^2 charges at 2.5 mA/cm^2, an 84% efficiency could be achieved over 45 cycles in carefully purified 1M $LiAsF_6$/PC electrolyte. This value was markedly superior to the best efficiency achieved in 1M $LiClO_4$/PC (65%), presumably due to the high purity of the $LiAsF_6$ salt, or the film-forming nature of AsF_6^- itself [15].

The utility of $LiAsF_6$ had previously been demonstrated by Dampier and co-workers in a series of static tests conducted at an elevated temperature (74 °C) [46]. Thus, Li was incubated with solutions of $LiAsF_6$ and (in decreasing order of stability) PC, methyl formate (MF), and methyl acetate (MA) at 74 °C. U.S. Steel Agri-Chemicals supplies a particularly pure grade of $LiAsF_6$, and its physicochemical properties have been recently reviewed [47].

Besides $LiAsF_6$ and $LiClO_4$, $LiBF_4$ has also been used in cycling the Li electrode in PC [14]. Other salts with sufficient solubility to be employed in secondary Li cells include $LiAlCl_4$, $LiPF_6$, $LiSbF_6$, LiO_3SCF_3, LiI, and LiSCN [48]. Purity of the salt and the chemical/electrochemical compatibility of the anion with Li are key considerations.

Recently, Exxon Research and Engineering Company has obtained several patents on a variety of organometallic anions suitable for Li secondary cells [49 - 51]. These anions typically comprise tetraalkyl and tetraaryl borates [49], borates including up to four unsaturated heteroatomic-containing ring substituents [50], and borate-containing halo-organic substituents along with alkyl and aryl radicals [51]. When dissolved in 1,3-dioxolane, some of these organoborate salts have been found to decompose when stored in the presence of TiS_2, however [49b].

5. "State of the art" aprotic-organic media for secondary Li cells

At present, two electrolytes show promise for cycling Li/TiS_2 cells: the $LiAsF_6$/2-Me-THF system of EIC Laboratories [52 - 54], and the $LiClO_4$/1,3-dioxolane system reported by Garth for use in a primary cell [55] and developed by Exxon in concert with their rechargeable TiS_2 cathode [31, 56, 57]. Problems associated with $LiAsF_6$/2-Me-THF are reaction of the AsF_6^- anion with Li, thus degrading both the electrolyte and its conductivity with time. A major stumbling block associated with $LiClO_4$/dioxolane is its propensity to detonate upon impact [49b, 58].

In order to avoid the explosion-prone ClO_4^- anion, an $LiAsF_6$/1,3-dioxolane medium has recently been reported on by Glugla [59]. He found that in this system the dioxolane reacted directly with Li, leading to rapid polymerization of the electrolyte. Accordingly, the $LiAsF_6$ electrolyte is inferior to that containing $LiClO_4$ in terms of cycling efficiencies.

TABLE 1

Li electrode cycling efficiencies in various electrolytes

Electrolyte	Charge Li (C/cm^2)	Discharge current density (mA/cm^2)	Anode efficiency (%)	Reference
1M LiClO$_4$/MA	10.0	5.0	65*	23
1M LiClO$_4$/PC	10.0	2.5	65**	45
1M LiAsF$_6$/MA	0.8	5.0	81*	60
1M LiAsF$_6$/PC	10.0	2.5	84**	45
1.5M LiAsF$_6$/THF	1.1	5.0	88**	38
1.5M LiAsF$_6$/2-Me-THF	1.1	5.0	96**	38
1.5M LiAsF$_6$/2-Me-THF	15 - 20	1.0	96 - 97**	54b
2.5 - 3.0M LiClO$_4$/1,3-dioxolane	40 - 60	10.0	>96***	56
2.5M LiAsF$_6$/DEE: THF (90:10, v/v)	1.1	5.0	>98**	61

*Average of the first 15 cycles on a Ni substrate: $E = Q_s/Q_p$, where s and p refer to stripping and plating.

**Average efficiency per cycle on a Li substrate;

$$E = \frac{Q_s - \dfrac{Q_{ex}}{n}}{Q_s}$$

where Q_s = charge stripped, Q_{ex} = charge of excess Li, and n is the number of "100%" cycles.

***Half-cell data in this electrolyte are unavailable. This efficiency value is a lower limit since the Li/TiS$_2$ cells were terminated prior to anode failure. The current density on charge was 2.5 mA/cm^2.

Comparing the cycling efficiencies of the Li electrode from one electrolyte to another is tenuous at best. Experimental parameters, the metal substrate, electrolyte purity, and (some would say) the Coriolis force, all affect cycling data. In Table 1, we cite efficiency values reported for several electrolytes in which the Li electrode is cycled in a half-cell and complete cell configurations. The most impressive efficiency values are those achieved by Exxon in an LiClO$_4$/1,3-dioxolane electrolyte [56]. However, safety considerations preclude the implementation of cells containing this shock-sensitive medium.

The use of LiAsF$_6$/2-Me-THF in practical cells requires that high cycling efficiencies be maintained for thick (>50 C/cm^2) charges of Li. While these anode efficiencies have not been reported in the open literature, we note that LiAsF$_6$/2-Me-THF has found use as an electrolyte in a variety of Li/TiS$_2$ cells. Thus, Holleck and co-workers have indicated that 500 mA h Li/TiS$_2$ batteries may be designed with a life of 100 - 200 deep cycles [52]; Malachesky reported obtaining 25 deep cycles in a 90 mA h/TiS$_2$ button cell

[53]; finally, Jet Propulsion Laboratory has tested 4.5 A h Li/TiS$_2$ D-cells [54a] and Globe Union has cycled 0.5 A h Li/TiS$_2$ cells [54b], all supplied by EIC Laboratories. In the latter cells, Rizzo reports that Li anode efficiencies of 96 - 97% could be achieved for cells cycled to 100% depth of discharge [54b]. The major problem limiting cycle life in these test cells was found to be short circuits, apparently caused by Li dendrite growth through the separator.

Most recently, a series of organic media comprising blends of diethyl ether (DEE) and other aprotic organic solvents has been developed by Koch [61]. In half-cell tests, these electrolytes outperformed LiAsF$_6$/2-Me-THF, and may replace it in the future.

6. Miscellaneous systems

In order to avoid the reactivity problems posed by placing Li directly in contact with a thermodynamically unstable organic solvent and salt, three alternative systems have been recently reported.

Eichinger has employed a solid electrolyte comprising LiI and C$_9$H$_{15}$ NO$_3$·CH$_3$I, where C$_9$H$_{15}$NO$_3$·CH$_3$I is the N-methylammoniumiodide of 2,6,10-triox-13-azatricyclo {7, 3, 1, 0} tridecane [62]. Although the conductivity of this material is of the order of that of pure LiI, implying a low rate system, reversible behavior of an Sb positive and a Li negative was reported.

Lazzari and Scrosati have reported on a rechargeable Li cell containing two intercalation electrodes of different activity [63, 64]. This obviates a metallic Li negative but trades off energy density for cycling efficiency.

7. Directions for future work

Normal temperature Li secondary batteries cycled at a moderate 5 - 10 h rate will most certainly require an electrolyte comprising an aprotic organic solvent and a Li salt. On this basis, we may identify known problems and suggest appropriate areas of research directed at solving them.

Given that all organic solvents are thermodynamically unstable toward Li, one can attempt to modify the kinetics of the rate-determining step of solvent reduction by Li. This requires the design and synthesis of molecules in which the activation energy of the slow step (presumed to be a one electron transfer from Li to the solvent) is sufficiently high. "Sufficiently high" really means that a cell incorporating such a solvent will deliver at least 100 deep cycles (5 - 10 h rate) at energy and volume densities of 90 - 100 W h/kg and 250 - 350 W h/l, respectively [65]. Alternatively, one might encourage a reactive solvent to form thin, coherent, Li$^+$-permeable films onto a Li substrate.

It is known that AsF$_6^-$, and ClO$_4^-$ react in the presence of Li [15, 43]; BR$_4^-$ (R = alkyl) reacts in the presence of TiS$_2$ [49]. Accordingly, new

organic, inorganic, or organometallic anions must be developed which are stable toward Li (or react in concert with the solvent to form a beneficial film) and ideally afford solution resistivities of no more than 200 ohm cm. In this regard, Exxon Research and Engineering has recently reported on utilizing the very stable closoborane anions of the form $B_{10}Cl_{10}^{2-}$ and $B_{12}Cl_{12}^{-2}$ in mixed solvent systems [66]. Alternatively, molten solvate salts comprising $LiPF_6$ and polyethers (glymes) may find use in very low rate secondary cells [67].

Understanding the nature of ion–solvent interaction in the bulk electrolyte as well as in the interfacial region is critically important to secondary Li technology. In this regard, multinuclear n.m.r. studies on ^7Li [68] and ^{13}C [38] enable one to investigate the degree of ion–solvent association. In a similar vein, Schmidt and Pons [69] have compared changes in infrared absorptions due to Li^+–solvent interaction with *ab initio* calculations [70], and have deduced that such interactions are ionic rather than covalent. Blomgren has recently employed solvent–solute donicities to determine ion pair formation constants yielding a good agreement between calculated and experimental values [71]. Measuring the rate constants for Li^+ reduction in different electrolytes [72] also provides thermodynamic information regarding free energies of solvation and, thereby, solvent–solute interactions. These fundamental studies will help elucidate conductance mechanisms, particularly in cases where mixed electrolytes manifest synergistic effects [73].

A fruitful area of research is concerned with how certain additives affect the bulk electrolyte and the Li surface. For example, crown ethers which selectively complex Li^+ ion have been shown to stabilize an $LiClO_4$/ PC electrolyte toward Li [74] as well as to raise its conductivity [75]. Additives which form beneficial films on the Li surface itself have been long sought after (*cf.* Section 3.2). Clearly, Li^+-permeable films are formed, but there is a paucity of information regarding their composition and structure. Studies employing e.s.c.a., Auger, s.i.m.s., etc., coupled with s.e.m./e.d.x. will be invaluable in obtaining these data. In this regard, JPL Laboratories has recently undertaken an e.s.c.a.–s.e.m./e.d.x. study of the native film on Li as received, and surface changes after cycling [76]. While Li is shipped from the supplier under Ar, both Li_2O and Li_2CO_3 were detected as surface contaminants. Although tedious and expensive, one cannot hope to understand the microchemistry of the Li electrode without resorting to these techniques.

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