Solubility problems relating to lithium battery electrolytes

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Abstract: Solubility phenomena in aprotic solvents commonly used for lithium-based cells and batteries have wide ranging effects on battery performance. Important properties relating to anode stability (passivation), general materials stability, conductivity, and operating temperature range are all dependent to a large degree upon solubility phenomena. Due to solvent reactivity with anode and cathode materials and due to the requirement that electrolyte systems must remain liquid and exhibit high conductivities over a wide temperature range, present research directions involve the use of mixed solvents. This research direction which has been largely empirical in nature has resulted in considerable success. By optimizing both solvent compositions and salt concentrations, relatively high stability lithium systems have become commercially available. The present paper reviews these advances and how they specifically relate to solubility phenomena.

Introduction: The basic electrochemical systems known prior to the 1900s include most of our presently known systems such as lead acid, nickel-cadmium, Leclanché, and fuel cells. Lithium batteries and to some extent nickel-hydrogen and nickel-metal hydride batteries are relative new comers to portable power sources with research starting around 1960. The promise of Li-based batteries is not only that of high energy densities, e.g. > 150 Wh/kg for commercial batteries compared to ~35 Wh/kg for lead-acid and nickel-cadmium systems, but also due to the fact that Li is much more environmentally friendly than either Pb or Cd. While considerable success has been made in commercializing Li-batteries, safety considerations are still a major problem limiting the sizes of batteries that can be offered to the public. A major factor influencing Li battery safety is the electrolyte solution. Since aprotic solvents are necessary for these batteries, flammability and toxicity are always major concerns. Having the limitation of the need for aprotic solvents, the next problems to be addressed are stabilities of electrode materials, particularly the anode, and ability to dissolve large quantities of lithium salts without precipitation as temperatures vary from -40°C for specialty batteries (~0°C for commercial batteries) to at least 50°C (or higher for electric vehicle application). Starting from around 1960 and continuing to the present day, a wide variety of aprotic solvents have been investigated, and a selected listing is given in Table 1 below. Inspection of this table immediately leads to important questions. With the exception of PC, EC, and 2CNP, the relative permittivities of the most important solvents are below 10 (solvents such as DMSI, TMSO and DMSO appear to be too reactive with Li for most practical applications). In spite of these low permittivities, it is generally observed that Li salts are surprisingly soluble in most solvents, particularly those containing carbonyl or carboxyl groups. Given that we can dissolve considerable quantities of Li salts in most of these solvents, the next considerations are those relating to solubility over a wide temperature range and the need to maintain concentrations of at least 1 mol dm^{-3} to prevent severe concentration polarization during battery discharge. In view of this problem, the concentration of most electrolytes for Li-based systems is almost always at least 1 mol dm^{-3} and, more commonly, between 1.5 and 3 mol dm^{-3}. Compared to aqueous systems, these are extremely highly concentrated solutions approaching those of molten salts or amorphous gels.

Electrochemical Cells: In this review, electrochemical cells of the following type are considered.

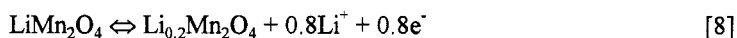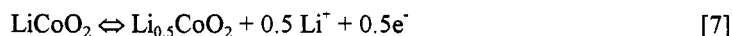| Li-based anode (-'ve Cu current collector)	liquid electrolyte	liquid or oxide cathode (+'ve Al current collector)	[1]

For the negative electrode, either metallic lithium or a lithium intercalating material are the materials of interest, and typical half-cell reactions of negatives considered in this review are:

$$Li \Leftrightarrow Li^+ + e^-$$ [2]

$$LiC_6 \Leftrightarrow 6C + Li^+ + e^-$$ [3]

$$8.4Li + SnO_2 \Rightarrow 2Li_2O + Li_{4.4}Sn$$ [4a]
$$Li_{4.4}Sn \Leftrightarrow Sn + 4.4Li^+ + 4.4e^-$$ [4b]

Metallic Li (eq. [1]) possesses the highest theoretical specific capacity of 3860 Ah/kg, but for safety and stability purposes, the intercalating anode materials LiC_6 and $Li_{4.4}Sn$ are the bases for present and future commercial cells: present day R&D is focusing on improvement of energy densities for these materials. Compared to metallic Li, the theoretical specific capacity of carbon-based anodes is 372 Ah/kg, and for $Li_{4.4}Sn$ the theoretical capacity exceeds 1100 Ah/kg (based on the Li/Sn atomic ratio of 4.4/1). In all cases the theoretical capacities of these materials are not realizable due to irreversible reactions with the electrolyte.

Various cathode materials are available for various applications, e.g. SO_2, $SOCl_2$ and MnO_2 for primary batteries, and for rechargeable systems, either metal halides such as $CuCl_2$, CuF_2 or metal oxides of Mn, Co and Ni. Representative half-cell reactions for primary and lithium cells based on these materials are:

$$2SO_2 + 2e^- \Rightarrow S_2O_4^{2-}$$ [5]

$$CuCl + e^- \Leftrightarrow Cu + Cl^-$$ [6]

$$LiCoO_2 \Leftrightarrow Li_{0.5}CoO_2 + 0.5\ Li^+ + 0.5e^-$$ [7]

$$LiMn_2O_4 \Leftrightarrow Li_{0.2}Mn_2O_4 + 0.8Li^+ + 0.8e^-$$ [8]

It is well known that practically all solvents used for primary and secondary Li batteries react with all anodes (eqs. [2-3]), and the stability of these anodes in nonaqueous media is due solely to an insoluble passive film produced by an irreversible chemical reaction. For primary Li cells such as that containing SO_2, the insoluble film is lithium dithionate, $Li_2S_2O_4$, which is spontaneously formed when Li is immersed in a solution containing SO_2. The corrosion reaction is identical to the cell reaction as derived from eqs. [2] and [5],

$$2Li(s) + 2SO_2(sln) \Rightarrow Li_2S_2O_4(s)$$
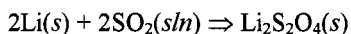
The fact that although Li is highly passivated, cells do pass considerable amounts of current indicating facile Li^+ transport through the film. To explain this behavior, Peled (1) offered the model of the solid-electrolyte interface which is shown in Figure 1. According to this model, a

Fig. 1. The Solid Electrolyte Interphase

non-porous *solid electrolyte interphase* (the SEI) is formed when Li is initially immersed in solution which is then followed by continual growth of a highly porous second layer. Li^+ ion transport through the SEI proceeds via solid state diffusion which, for thin SEI films, is rapid, and transport through the porous layer is governed by solution conductivities and tortuosity of the channels within this porous layer. In primary Li/SO_2 cells, the need to maintain high solution conductivities at very low temperatures (to -40°C) is accomplished by adding acetonitrile to the electrolyte. While metallic lithium reacts quickly with acetonitrile producing methane and LiCN, in the presence of SO_2 the solubility of the dithionate is so small that the SEI protects the anode and self-discharge (due to Li oxidation) is negligible. In fact, the shelf life of these cells is at least 10 years. For
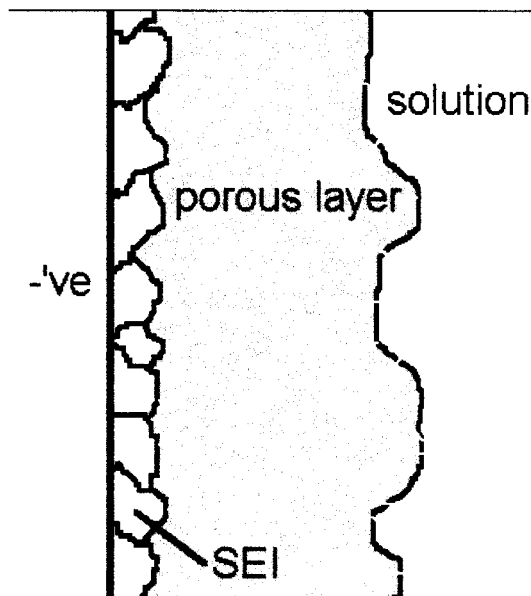
rechargeable Li cells, metallic lithium presents numerous problems leading to very poor cycle life. The passive film breaks down and reforms continuously upon cycling, and dendrite formation is excessive leading to internal cell shorting and failure. Although energy densities are lower, the use of Li-intercalating anode materials such as hard and soft carbons instead of metallic Li avoids these problems and are now the bases for commercially available Li-ion cells. Tin oxides are presently being investigated in numerous laboratories worldwide for possibly replacing LiC_6 anodes. As with metallic lithium, Li-intercalating anodes are also highly active (thermodynamically unstable in aprotic solvents) and undergo corrosion followed by the formation of a stable (insoluble) passive film. Corrosion and passivation are easily confirmed by simple coulombic "titration" measurements which are discussed below.

Table 1. Properties of selected solvents (25°C unless stated otherwise)

solvent	ε	η/cP	solvent	ε	η/cP
toluene	2.379	0.552	2-cyanopyridine (2CNP, 30°C)	93.77	1.832
dimethyl carbonate (DMC)	3.12	0.585	tetrahydrofuran (THF)	7.39	0.46
diethyl carbonate (DEC)	2.82	0.748	dimethoxymethane (DMM)	2.71	0.329
ethylmethyl carbonate (EMC)	2.4	0.65	dimethoxyethane (DME)	7.15	0.402
propylmethyl carbonate (PMC)	2.8	~0.75	dimethyl sulfite (DMSI)	20.80	0.8732
propylene carbonate (PC)	64.92	2.53	tetramethylene sulfone (TMSO, 55°C)	43.3	10.29
ethylene carbonate (EC, 65°C)	89.6	1.85	dimethyl sulfoxide (DMSO)	46.68	2.016
γ-butryolactone (γ-BL)	41.77	1.727	dimethylformamide (DMF)	36.71	0.794
methyl formate (MF)	8.90	0.328	SO_2 (0°C)	15.35	0.403
methyl acetate (MA)	6.67	0.368	thionyl chloride ($SOCl_2$)	8.68	0.640

For safety reasons as well as commercial processing, Li-ion cells utilizing a Li-intercalating anode are constructed in the discharged state. Cells with both Li-intercalating anodes and cathodes are commonly referred to as "Li-ion cells" since only Li^+ is transported across the cell during charge and discharge. For example, the cell C|electrolyte|$LiCoO_2$ constructed in the discharged state must first be charged before the cell can be used. The charging reaction which is the reversie of discharging (eqs. [2] & [7]) is

$$6C + LiCoO_2 \Leftrightarrow Li_xC_6 + Li_{1-x}CoO_2$$
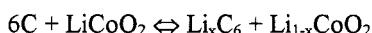
and a typical first charge is shown in Figure 2. Note that the charge consumed on the first charge, 420 Ah/kg, exceeds the theoretical capacity of 372 Ah/kg for LiC_6

Fig 2. Potential – capacity curve for a graphite anode during the first charge/discharge cycle.

by around 12 %. This irreversible loss in capacity is entirely due to solvent/electrolyte decomposition (reduction) to numerous insoluble products forming the passivating layer at the carbon anode. The delivered capacity upon the discharge, 370 Ah/kg, is very close to theoretical, but subsequent cycling will
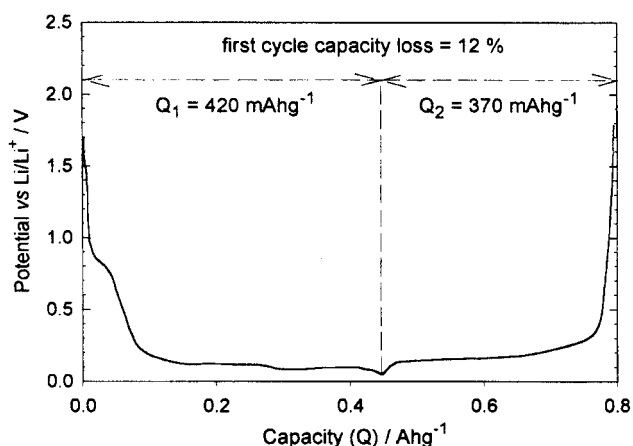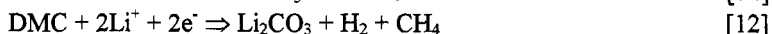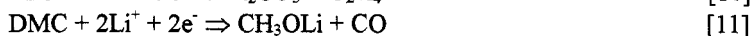
continue to result in smaller irreversible losses until a stable passive film is completely formed. Normally, 5 to 10 charge/discharge cycles are required until a reversible situation is achieved at which point the Li_xC anode will cycle reversibly at ~250 to 325 mAh/g for hundreds of cycles (i.e., $x \approx 0.6$ to 0.9 in Li_xC_6). The composition of the insoluble passive films on both metallic Li and LiC_6 is quite complex and the subject of many investigations starting in the 1970s. These early studies (2-4) which mainly employed ethers, esters and PC as the solvent and $LiAsF_6$ as the electrolyte clearly identified LiF and other complex products of As such as Li_3As and, more recently, As° reported by Aurbach et al. (5). It is believed that formation of these insoluble surface films are the result of the formation of Lewis acids from the anion,

$$LiAsF_6 + 2Li^+ + 2e^- \Rightarrow AsF_5\cdot + 3LiF \qquad [9]$$
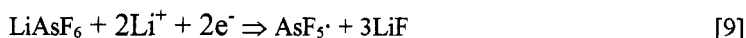
followed by irreversible chemical and electrochemical reactions. In 1989 Plichta et al. (6, 7) reported that additions of dialkyl carbonates such as DMC and DEC (see Table 1) and CO_2 resulted in significantly increased stability and improved cyclability at Li anodes, and based on earlier work by Aurbach et al. (8), it was assumed that these improvements were due to the formation of insoluble carbonates on the anode surface. Based on these findings (6, 7), almost all present day electrolyte formulations for rechargeable Li and Li-ion cells now incorporate DEC, DMC EMC and EC in some propriety combination. In electrolyte solutions containing one or more of these carbonates, the predominant passive films on the anode surface are solvent decomposition (reduction) products. The recent studies by Aurbach et al. (e.g. 9 and references cited therein) using in situ spectroscopy have identified Li_2O, Li_2CO_3 and $ROCO_2Li$ species as components of these passive films. Li oxides, carbonates, and alkoxides have also been found on LiC_6 sufaces by Yoshida et al. (10) who also reported gas evolution (CO, CH_4, C_2H_4, H_2) on initial charging of these anodes. According to Yoshida et al., the mechanisms proposed for formation of insoluble films are

$$EC + 2Li^+ + 2e^- \Rightarrow Li_2CO_3 + C_2H_4 \qquad [10]$$
$$DMC + 2Li^+ + 2e^- \Rightarrow CH_3OLi + CO \qquad [11]$$
$$DMC + 2Li^+ + 2e^- \Rightarrow Li_2CO_3 + H_2 + CH_4 \qquad [12]$$
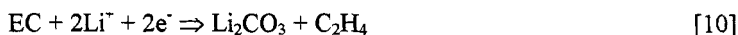
According to Aurbach et al., the mechanisms for solvent reduction can also involve radical formation, e.g.

$$EMC + Li^+ + e^- \Rightarrow CH_3CH_2OLi + CH_3OCO\cdot \qquad [13]$$
$$CH_3OCO\cdot + e^- \Rightarrow CH_3OLi + CO \qquad [14]$$
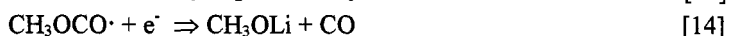
It is noteworthy that while the solubilities of these fluorides, oxides and carbonates appear to be negligible, no quantitative solubility data exists for these compounds.

In the search for Li-intercalating anode materials with improved specific capacities over LiC_6, Idota et al. (11) at Fujifilm Celltec found that tin oxides (e.g. SnO and SnO_2) can reversibly insert more than twice the amount of Li than hard and soft carbons. The amounts of lithium which can be inserted into these materials exceeds 4 Li atoms per Sn atom. Idota et al. incorrectly assumed the mechanism to be that of simple intercalation into the oxide. However, noting that this is an unusually large amount of lithium for
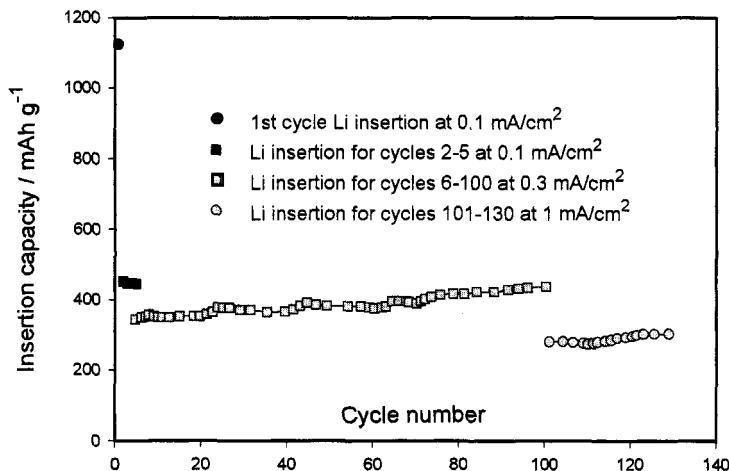

Fig. 3. Insertion capacity of SnO_2 thin film (700 nm) electrolyte: 1 M $LiPF_6$ in 1:1 (vol) EC:DMC

an intercalation process, and that the phase diagram for the binary Li/Sn system (12) shows 8 distinct Li/Sn phases, the maximum being $Li_{22}Sn_5$ (i.e. $Li_{4.4}Sn$), Courtney and Dahn (13) using *in situ* X-ray spectroscopy confirmed that the mechanism was reversible alloying of Li (eq. [4]) rather than intercalation. This mechanism was later confirmed by Brousse *et al.* (14). As with LiC_6 anodes, the SnO_2 anode is stabilized by an insoluble Li_2O firm formed upon initial charging as shown in Fig. 3 (data from ref. (14)). On the first charging cycle, it is seen that the insertion capacity exceeds 1100 Ah/kg, but on the first and subsequent discharges and charges, only about 400 Ah/kg is reversibly alloyed and dealloyed in and out of the anode. This corresponds to a huge irreversible (i.e. loss in) capacity of ~60 % in formation of the stable passive film on Li_xSn. While reversible capacities of ~400 Ah/kg are observed over hundreds of cycles, the major problem with this system is that all of the lithium alloyed into Sn comes from the cathode, e.g. $LiCoO_2$, which would require excessive amounts of cathode material to balance this Li-ion cell.

From the mid 1960s to the 1970s, considerable attention was given towards the development of rechargeable Li cells using metal halide electrodes: e.g. the Li/CuCl cell (see eq. [6]) has an attractive theoretical energy density of 685 Wh/kg. However, in several previous reviews (15, 16) it was shown that the failure to build practical Li cells with metal halide cathodes is due to dissolution of the cathode upon discharge; i.e. one reaction product is the halide ion (eq. [6]) which forms very stable complexes such as $CuCl_2^-$, $CuCl_3^{2-}$, $Cu_2Cl_4^{2-}$ and $Cu_3Cl_6^{3-}$ (17). Our experience (15, 16) is that while the solubility products of metal halides are much smaller in aprotic organic solvents than in water, the stability constants for the complexes are much larger resulting in significant dissolution of the metal halide cathode followed by rapid transport to and self-discharge at the anode. With the introduction of lithium-intercalating metal oxide cathodes, e.g. eqs. [7-8], the problem of soluble cathodes has been practically eliminated, but with new problems involving dissolution of electronically conducting grid materials. One example involves the use of $LiCoO_2$ cathodes. This material was originally synthesized by Mizushima *et al.* (18) who also demonstrated the possibilities of this material (eq. [7]) as a cathode for rechargeable Li cells in propylene carbonate solutions. The practicality of using $LiCoO_2$ in commercial Li cells was first demonstrated by Plichta *et al.* (6, 7, 19) by use of ultrastable solvents (6, 7) and replacement of Ni grid materials with Al (6, 19). In solutions containing $LiAsF_6$ electrolytes, Al grids were found not to undergo corrosion, but the concern for use of As compounds in commercial cells is the basis for the search of stable electrolytes to replace $LiAsF_6$. A most promising replacement is the imide LiIm, lithium tris(trifluoromethanesulfonyl) imide, $LiN(SO_2CF_3)_2$ first synthesized by Armand *et al.* (20). This salt has improved transport properties (21, 22) and is thermally stable, but was subsequently found to corrode Al grids at all potentials above 4.0 V *vs.* Li/Li$^+$ (23). Figures 4 and 5 show the effects of potentiostating Al
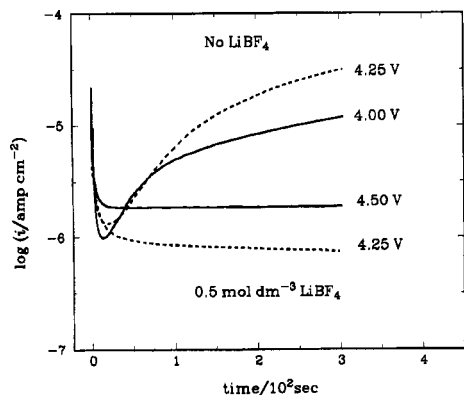
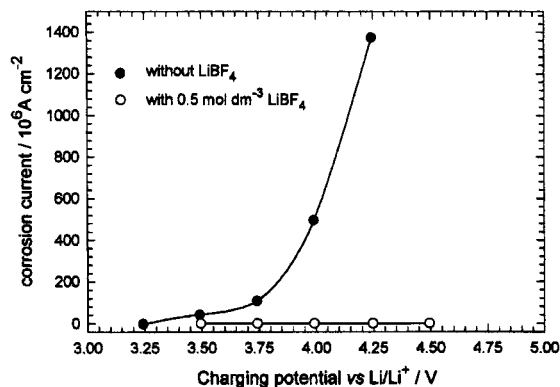Fig. 4. Current-Time plots at Al electrodes in 1 mol dm^{-3} LiIm in PC:EC:DMC

Fig. 5. Corrosion currents at Al electrodes in 1 mol dm^{-3} LiIm in PC:EC:DMC

wire electrodes at positive potentials in $LiN(SO_2CF_3)_2$ solutions in the absence and presence of $LiBF_4$. In solutions without $LiBF_4$ additions, the protective film on Al breaks down at potentials above 3.25 V *vs.* Li/Li$^+$. Surface spectroscopy (e.g. X-ray photospectroscopy) have identified Al_2O_3 as the initial pasive film on Al, and AlF_3 as the passive film formed in the presence of AsF_6^- and PF_6^- salts (24), and more

recently LiF (25). Mechanisms on the breakdown of Al_2O_3 surface films and formation of AlF_3 and/or LiF on the Al surface have not been established.

Electrolyte Solutions: Experience over the last 15-20 years has shown that Li battery systems with cell voltages $\geq$ 4 V should contain EC and/or an alkyl carbonate (e.g. DMC, DEC, EMC) as a solvent component. In fact, all Li-ion cells commercially available at the present time contain at least two of these solvents in either binary, ternary or quaternary mixtures (26). It is also probable that a fluoride salt should be employed as an electrolyte component to prevent corrosion of grid materials at high positive potentials. Commercial Li-ion cells use $LiPF_6$ as the preferred electrolyte since it is highly conductive and, we believe, environmentally friendly. However $LiPF_6$ is expensive and thermally unstable, extremely hydroscopic (HF is a hydrolysis product), and for these reasons $LiBF_4$, $LiAsF_6$ and to some extent $LiClO_4$ still are considered as practical electrolytes. The search for new and highly stable electrolytes have resulted in highly conductive and thermally stable salts such as the imide LiIm discussed above, lithium methide or LiMe (tris(trifluoromethanesulfonyl) methide), $LiC(SO_2CF_3)_3$ developed by Dominey (27), and the new class of lithium organoborates presently under development by Barthel *et al.* (28). In all cases, the major objectives are to develop electrolyte solutions which are thermally and electrochemically stable, and which have high solubilities required to yield solutions with electrolytic conductivities $> 1 \cdot 10^{-3}$ S cm^{-1} over a wide temperature range of around -20°C to around 50°C. Special applications by the military and space exploration agencies require solutions with the same conductivities from -40°C or below to 70°C. While qualitative solubility data are available for a number of these salts in several recent papers (see below), quantitative solubility data are almost non-existent. What is known is that esters, ethers and other solvents can dissolve large quantities of salts. Ebner (29) reported physical properties for $LiClO_4$ and $LiAsF_6$ in PC and MF solutions, and although the solubility of $LiAsF_6$ in PC probably exceeds 4 mol dm^{-3}, Ebner's study demonstrates the effectiveness of solvents such as PC and MF to dissolve very large amounts of Li-salts. For a 3.11 mol kg^{-1} solution of $LiAsF_6$ in PC, there are 9.80 moles of solvent per mole of salt, and assuming the solvation number of Li^+ is at least 3 (it is probably closer to 4, e.g. see ref. 30) and that for the anion is one or less, at least for moles of solvent are required to solvate 1 mole of salt. Clearly, not much free solvent is available for additional solvation, and the solution while liquid is thus approaching that of a molten salt (the viscosity of this system is extremely high: 4.12 P). For comparison, note that a 3.11 mol kg^{-1} solution in water contains 55.5 moles of H_2O per mole of salt. A recent study by Choquette *et al.* (31) confirms the complexity of these aprotic electrolyte solutions and is one of the most complete solubility studies for several systems of interest for lithium batteries. Choquette *et al.* reported the solubility of LiIm in a series of sulfamides and glymes, and their data for the imide salt, LiIm, in dimethoxyethane are shown in Fig. 6. The solubility of LiIm in DME is extremely high, and the two stable solvates LiIm·3DME and LiIm·DME melt congruently at 29°C and 58°C, respectively. DME also forms stable 1:2 solvates with $LiAsF_6$, $LiBF_4$ and $LiClO_4$ (31). At high concentrations, these solutions are certainly highly associated, but due to the difficulty in identification of all species present in solution, little data appear in the literature. For more dilute nonaqueous electrolyte solutions from around 0.1 to 0.5 mol dm^{-3}, ion pairs, dimers, triple ions, tetramers and higher aggregates have been reported (e.g. see 15, 16, 32-34). The formation of these aggregates have direct effect on both conductivities and solubilities, and studies such as those reported in (31) are of importance in defining and understanding the physical and chemical properties of these solutions.

Figure 6. Binary phase diagram for $LiN(SO_2CF_3)_2$ in dimethoxyethane.

L = liquid
A = solid DME
B = $LiN(SO_2CF_3)_2$·3DME
C = $LiN(SO_2CF_3)_2$·2DME
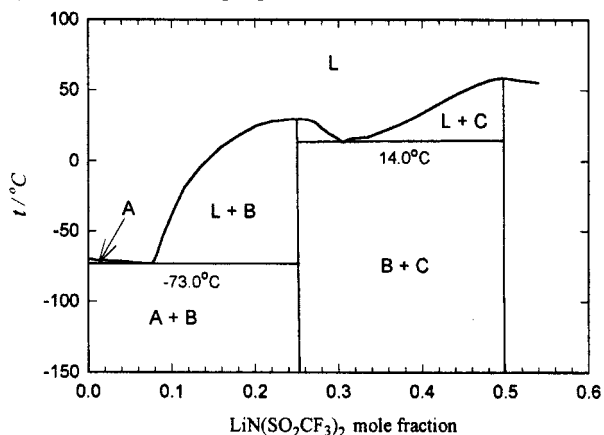
An important property of these highly concentrated solutions is that they are liquid down to very low temperatures (e.g. see Fig. 6) which, providing conductivities are sufficiently high, enables useful capacities to be obtained from Li cells at very low temperatures. There are numerous efforts in progress for developing low temperature capable electrolyte solutions, and some representative recent data are given in Table 2. As a result of these studies, numerous but qualitative solubility data have been determined. The major approaches for developing conductive electrolyte solutions at temperatures $\leq$ -40°C without precipitation of the electrolyte involve the use of mixed solvents. The bases for selection of specific solvents used in these mixtures are (see Table 1) high dielectric constant to minimize ion association, some carbonate solvent to insure the formation of stable passive films on the anode, presence of carbonyl or ether groups which are effective in dissolving Li-salts, low viscosity required for high conductivities at low temperatures, and varying solvent composition to prevent phase separation at low temperatures.

Table 2. Liquid electrolyte conductivities as a function of temperature[a]

	-65°C	-50°C	-40°C	-20°C	0°C	25°C	40°C
LiPF$_6$ - EC:DMC:DEC (5:4:1 vol)			s	2.83	5.91	10.87	14.18
LiPF$_6$ - EC:DMC:DEC (1:1:1 vol)[c]		s	nd	2.90	5.71	10.01	12.79
LiPF$_6$ - EC:DMC:DEC (1:1:1 vol)	0.02[b]	nd	1.01	2.9	5.6	9.7	nd
LiPF$_6$ - EC:DMC:MA (1:1:1 vol)	0.140	0.680	1.83	5.79	9.88	15.81	19.13
LiPF$_6$ - EC:DMC:EMC (1:1:1 vol)	s	0.680	1.40	3.32	6.28	10.82	nd
LiPF$_6$ - EC:DMC:EMC (2:2:1 vol)[c]			s	3.17	6.24	10.93	~16
LiPF$_6$ -EC:PC:DMC (1:1:3 vol)			s	2.43	6.54	11.28	~15
LiPF$_6$ - EC:DMC (1:1 vol)				s	~4.4	11.1	~15
LiAsF$_6$ - EC:PC (7:3 vol)[d]			s	1.38	3.45	~7	10.23
LiAsF$_6$ - EC:PC:DME (2.5:2.5:5)[d]			s	0.01	0.63	~3	6.95
LiIm - EC:DME (1:1 vol)[d]				s	5.46	~13	16.58
LiIm - EC:PC (1:1 vol)[d]		s	0.28	1.21	2.80	~6	7.69

[a]All concentrations are 1 mol dm^{-3} and data are from MaxPower (unpublished) unless stated otherwise. Conductivity units are 10^{3}S cm^{-1}. In the table, s indicates freezing of the solution, and nd indicates not determined. [b]-60°C. [c]Ref. 35. [d]Ref. 36.

An emerging concept for increasing solubilities and simultaneously increasing solution conductivities is the use of cation-coordinating ligands such as crown ethers and cryptands (e.g. see refs. 37, 38). Crown ethers such as 15-crown-5 (15C5) and 18C6 are very effective in hosting Li$^+$ ions according to

$$Li^- + CE \Leftrightarrow (LiCE)^+ \qquad [10]$$

In addition to increasing solubilities (e.g. in solvents containing a hydrocarbon or halocarbon), complexes such as (Li-15C5)$^+$ and (Li-18C6)$^+$ often exhibit greater mobilities than the highly solvated (uncomplexed) Li$^+$ ion which results in higher transport numbers for the (LiCE)$^-$ complex cation (e.g. see 37 and 38 and references cited therein). The increase in transport numbers is significant, up to 20 % in some cases, and is important in minimizing concentration polarization which is a major factor leading to very poor Li-ion cell performance at temperatures below -20°C (39). While technology based on these findings has not yet been fully explored, it is anticipated that future research will lead to improved Li-ion cell performance.

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