# Lithium Salt Solutions in Mixed Sulfone and Sulfone-Carbonate Solvents: A Walden Plot Analysis of the Maximally Conductive Compositions

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ABSTRACT: In seeking solutions to the problem of the high viscosity of electrochemically stable sulfone electrolyte solvents for high voltage lithium cells, we have explored a number of binary sulfone + cosolvent systems, including all-sulfone cases. We report systems that at 55 °C are nearly as conductive as the "standard" carbonate-based electrolyte and may merit further study. We employ a plot based on the classical Walden rule as a primary tool for assessing the loss of potential conductivity to undesirable ion-pairing phenomena. To conclude, we briefly consider the possible alternatives to molecular solvent-based electrolytes for high voltage cathode cells.
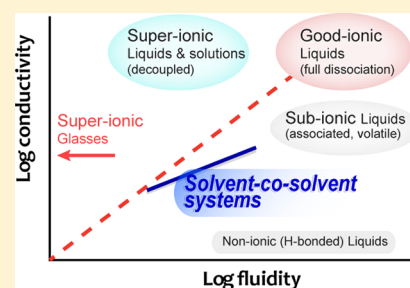
INTRODUCTION

In recent years, the classical Walden rule has found new application as a fruitful approach to assessing the state of ionization of ionic liquids and classifying different types of ionic conductors among superionic, good ionic, and subionic systems.[1−3] It has been established that the deviation of experimental data on viscosity and conductivity from the ideal Walden line provides an assessment of ionicity for these systems that correlates very well with the more demanding analyses based on experimental determination of deviations from the Nernst−Einstein equation.[3,4] A generic diagram of this type is reproduced from early work[5] in Figure 1. The *superionic* example is taken from studies on liquid $LiAlCl_4$ (T_m = 145 °C) in which the Li^+ ion moves faster than expected from

Figure 1. Walden Plot for ionic liquids, molten salt, and hydrate systems. The ideal line position is based on the properties of dilute aqueous KCl solution. Note the superionicity of the liquid hydrate.

viscosity (though not as extremely as in the previously cited case[6] of a silver halide glassformer of exceptional *ambient* temperature conductivity, ∼100mS/cm). One of the *subionic* examples is an aprotic ionic liquid tetrafluoroborate (with tetralkylammonium type cations)[2] that at first sight would be expected to be a high ionicity system, illustrating that high ionicity cannot be taken for granted. The extreme subionic case of α-picoline + acetic acid[1] dates back to the first work on protic ionic liquids in which Ramsay (1876)[7] reported "no reaction" for this system.

This approach to assessing ionicity should also be useful for monitoring the compromises involved in increasing the conductivity of solutions of lithium salts in high dielectric constant solvents by the addition of lower viscosity but less dissociating solvents; however, it seems not to have been applied in this way in any recent studies.

An example of the quick assessment of different lithium salts in high dielectric constant solvents made possible by use of the Walden plot is provided by the data in Figure 2 in which conductivity and viscosity data for lithium salts in sulfolane (tetramethylene sulfone (TMS), ε_s = 43) reported by Kolosnitsyn et al.[8] are presented in this form and then compared with the single point available for the "standard DOE" lithium battery electrolyte (1 M $LiPF_6$ in EC/DMC (1:1), first developed by Tarascon and Guyomard.[9] Here EC is ethylene carbonate and DMC is the acyclic low viscosity dimethylcarbonate. (See Scheme 1.)

It is not surprising to find, in Figure 2, that (the favored) $LiPF_6$ is the only one of the three salts of superacids that behaves as an ideal Walden electrolyte in the solvent sulfolane. The 1 M solution of LiTf evidently loses more than 60% of its
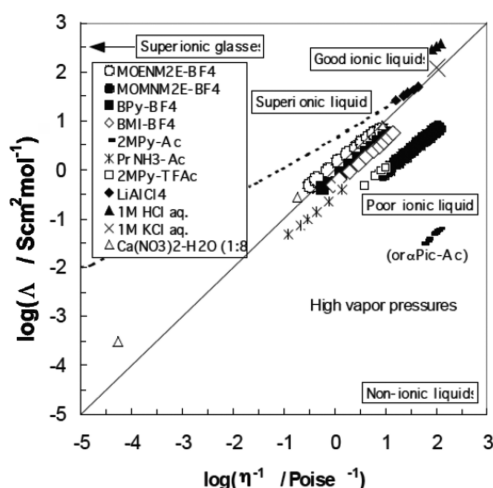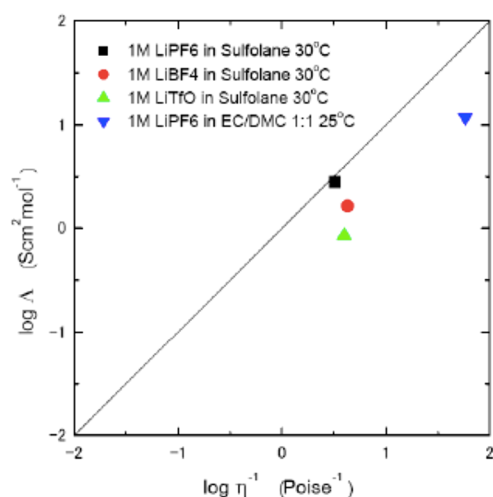
Figure 2. Walden plot presentation of data from ref 7 showing lowered ionicities for all except LiPF$_6$, including the standard Li battery electrolyte.

potential conductivity to ion pairing. More interesting perhaps is that a similar, indeed greater, disadvantage attends the dissociation of LiPF$_6$ in the standard electrolyte (shown as a blue inverted triangle in Figure 2) based on viscosity, conductivity, and density data from Lee et al.[10] Assuming that LiPF$_6$ in EC is fully dissociated, as in TMS, this point tells us that half of the ~ one order of magnitude increase that should have followed the increase in fluidity obtained by the DMC addition has been lost to ion pairing.

Not shown in Figures 1 or 2 (but to be discussed below) is an additional interesting, and at first sight unexpected, feature that characterizes poorly dissociated ionic solutions. This is the feature utilized in a previous study[11] to show the distribution of dissociating abilities among lithium salts of superacids to highlight the favorable properties of the new salt LiBOB. This was the existence of an actual maximum in the conductivity

versus temperature relation that is found when even highly ionic salts are dissolved in low dielectric constant solvents. Of the four salts LiTf, LiClO$_4$, LiTFSI, and LiBOB, only LiBOB and LiTFSI avoided this maximum when the solvent was dimethoxyethane (DME), $\varepsilon_s \approx 5$. (LiPF$_6$ was too insoluble in DME to be included in the study).

The present work was undertaken to again study the use of low viscosity solvents for increasing the conductivity of some highly dissociating, but undesirably viscous, solvents. These are solvents that are highly oxidation-resistant and so are of interest in connection with the development of electrolytes capable of supporting 5 V cathodes such as the much-researched LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode. Previous work[12] had shown that the acyclic sulfone ethyl methyl sulfone (EMS) (see Scheme 1), studied both on platinum and at the Li$_{(1−x)}$Mn$_2$O$_4$ cathode, could withstand 5.9 V relative to Li/Li$^+$ before important oxidative current started to flow, whereas TMS long known for its electrochemical stability, could withstand 5.5 V under the same conditions. It appeared that these solvents might become solvents of choice for matching with 5 V cathodes if their lithium solution conductivities could be made high enough, either by chemical manipulation or by additions of appropriate low-viscosity solvents.

Chemical manipulation seemed rather successful in one case reported previously[13] in which the reduction of viscosity had been achieved by DMC additions to the partially fluorinated sulfone, 1,2,3-trifluoropropylmethylsulfone (FPMS). (See Scheme 1.) A surprising transfer of oxidative stability to the DMC cosolvent (now explained by the simulations of Borodin and coworkers[14] showing preferential alignment of sulfone over carbonate at the cathode surface) was reported. Although conductivity of this solution had seemed high when judged by indirect means,[13] subsequent preparation of the sulfone in quantities sufficient for adequate conductivity measurements yielded disappointing results.[15] Evidently FPMS would not make the appropriate sulfone starting point even though the

Scheme 1. Chemical Structures of Solvents and Cosolvents

☐ **Solvents**

Name	Source	Chemical structure	Abbreviation	T_m (°C)
Dimethyl sulfone	TCI >99%		DMS	110
Ethylmethyl sulfone	synthesized		EMS	36.5
Tetramethylene sulfone (Sulfolane)	Aldrich 97%		TMS	27
Fluoromethyl sulfone	Aldrich 98%		FMS	—
Trifluoropropylmethyl sulfone	synthesized		FPMS	56

☐ **Co-solvents**

Ethylene carbonate	FERRO >99%		EC	36.4
Dimethyl carbonate	FERRO >99%		DMC	4.6

behavior of LiPF$_6$ in mixed solvents of this sulfone + DEC at the graphite anode was very favorable.[13]

Therefore, the route of exploration by alternative low-viscosity diluent additions has been followed. Abouimrane et al.[16] have recently shown that encouraging performance of cells with titanate anodes (to avoid the graphite exfoliation and general safety problems) and LiNi$_{0.5}$Mn$_{1.5}$O$_2$ cathodes can be obtained when LiPF$_6$ in sulfolane with carbonate cosolvents is used as the electrolyte. We have sought information on the possibility that all-sulfone electrolytes of the same class might be even better. The choice of low-viscosity sulfones is, however, very limited (if we exclude the chlorinated cases). There are only three possibilities, perfluoromethyl methyl sulfone (CF$_3$SO$_2$CH$_3$), perfluorinated dimethyl sulfone ((CF$_3$)$_2$SO$_2$), and CH$_3$SO$_2$F, normally known as methane sulfonyl fluoride which, for this article, we will call fluoromethyl sulfone (FMS) (Scheme 1) . Therefore, to round out the study, some nonsulfone second components have been included.

■ EXPERIMENTAL SECTION

All chemicals used, except FPMS, were commercially available (Scheme 1) and were used without further purification. FPMS was synthesized in house by a modification[17] of the procedure described in ref 13.

Viscosity measurements were performed using a Cannon-Manning viscometer, which was calibrated by the manufacturer. The temperature was controlled to ± 0.1 °C by means of a water circulating bath (LC20, Lauda). Viscosity values of some electrolyte solutions were measured by a Stabinger viscometer (SVM3000, Anton Parr).

Solution densities were measured with accuracy sufficient for obtaining equivalent conductivities for our Walden plots (∼1%) simply by measuring the weight of the sample filling a 1 mL volumetric flask at different temperatures. Before each measurement, the flask was maintained in an aluminum block at the desired temperature for 0.5 h to obtain a uniform temperature.

Ionic conductivities were measured by the standard complex impedance method, using a PARSTAT2273 apparatus (Princeton Applied Research) with a frequency range of 10 Hz to 1 MHz. The electrolytes were contained in a dip-type cell with twin platinum electrodes. The cell constant of 0.59 cm^{-1} was determined using 0.01 M KCl aqueous solution. The temperature was controlled by a Peltier temperature controller with an aluminum block for lower temperature and a thermostatted chamber (DKN402, Yamato) for higher temperature.

To evaluate suitability for high voltage applications, we carried out linear sweep voltammetry using a potentio/galvanostat (PARSTAT2273) at room temperature. A cylinder-type cell with Pt plate as working electrode and Li metal as counter and reference electrodes was used for the measurements.

■ RESULTS

Methyl trifluoromethyl sulfone is capable of dissolving LiTFSI, but the methyl protons become strongly activated in the presence of so much electron-withdrawing power, to the extent that hydrogen is rapidly liberated in the presence of lithium metal. The perfluorinated dimethyl sulfone was very fluid but had little solvent power. Finally, FMS proves to be a solvent for LiTFSI and more weakly, LiPF$_6$. For LiTFSI, the conductivity is

shown in Figure 3, where it is clear that it is a low ionicity solution and barely worthy of further study, especially in view of its toxicity.
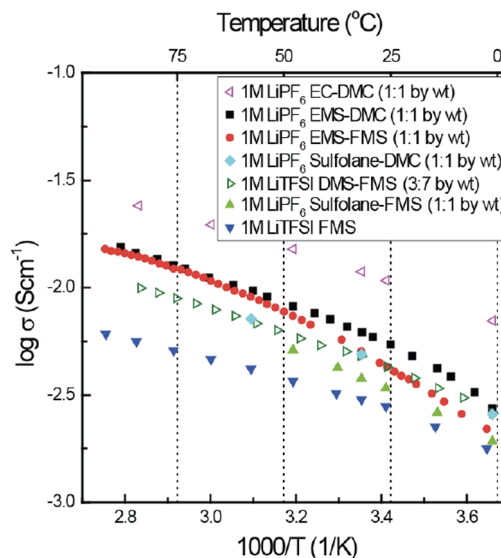

Figure 3. Conductivities of 1 M Li salts in the single solvent fluoromethyl sulfone (methane sulfonyl fluoride) and of various sulfone-based mixed solvent systems, as designated in the Figure legend.

Despite these disadvantages, it was decided to explore its performance as a cosolvent. Conductivities of solutions of LiPF$_6$ in EMS and sulfolane, with FMS, and also EMS-DMC, each at mass ratios 1:1, are shown in Figure 3, along with data for the mixed solvents EMS-FMS, EMS-DMC, and sulfolane-FMS.

The conductivities of the EMS-based solutions are quite respectable, approaching 10 mS/cm at 55 °C, where many assessments of cell performance are made. Because this is not much less than the conductivity of the standard electrolyte at 55 °C, it is certainly of interest to explore its half-cell and full-cell behavior in more detail. This is only done in a separate paper[18] because the present article is focused on the description of the electrolyte physical chemistry, but the stability against oxidation on Pt is shown here (Figure 4). Whereas FMS as single solvent is oxidized above 5.5 V, its solution in sulfolane, evaluated by linear extrapolation to zero current of the steeply rising plot, is rather stable. The steeper rise reflects the higher
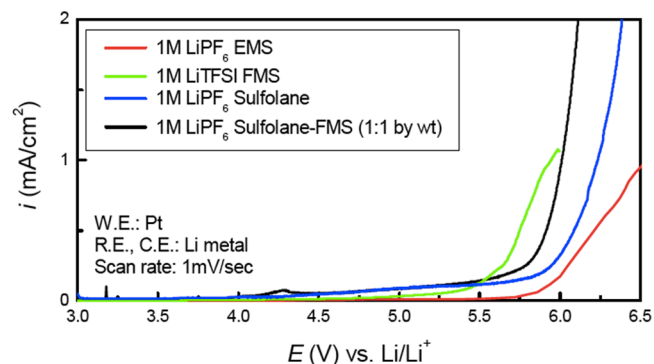

Figure 4. Linear sweep voltammetry determinations of oxidative stability on Pt for the various solutions of Figure 3.

conductivity. Concerning FMS, we note here that it has excellent SEI (solid−electrolyte interface)-forming propensity on graphite,[18] perhaps because it has the same $[FSO_2]^-$ moiety as the $[FSA]^-$ anion of the lithium bis-fluorosulfonylamide salt LiFSA, which is known for this SEI-forming property.[19]

The key question, now to be answered, is how effective the FMS has been in its intended role as a conductivity enhancer for the parent sulfones, EMS or TMS.

For this purpose, we show in Figures 5 and 6 viscosity data for solutions of $LiPF_6$ in sulfolane + FMS and for the separately
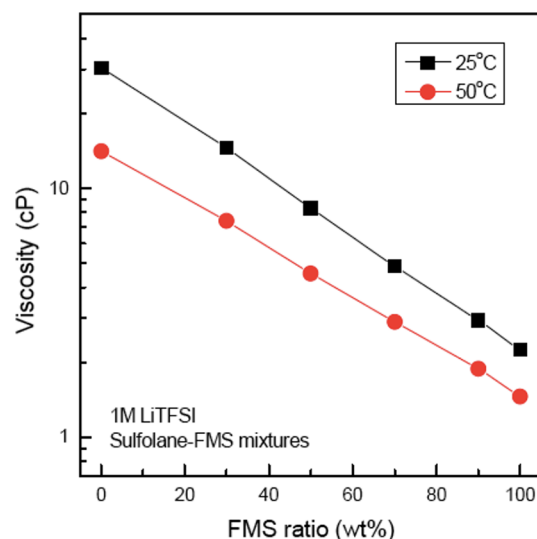
Figure 5. Viscosity versus cosolvent content plots for sulfolane−binary solutions: sulfolane + fluoromethylsulfone.
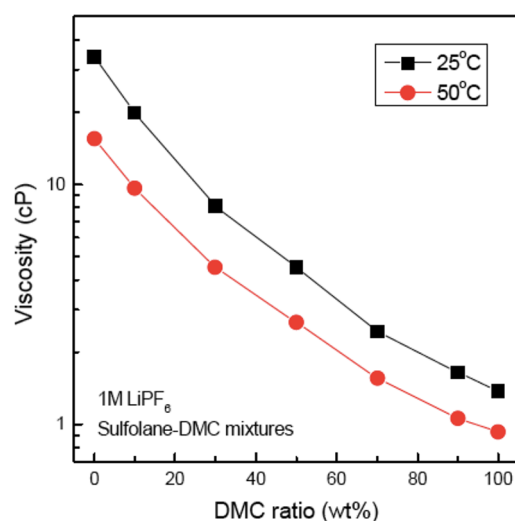
Figure 6. Viscosity versus cosolvent content plots for sulfolane−binary solutions: sulfolane + dimethylcarbonate.

interesting system sulfolane + DMC studied by Amine and coworkers.[16] The decrease is log linear in the all-sulfone case and exponential in the mixed system, presumably as a consequence of less ideal mixing in the latter case.

Figure 7 shows the conductivity variations for the 1 M LiPF6 in the sulfolane-−DMC case, and it is clear that the conductivity increase is much less than would be expected from the order of magnitude decreases in viscosity for the same DMC content.
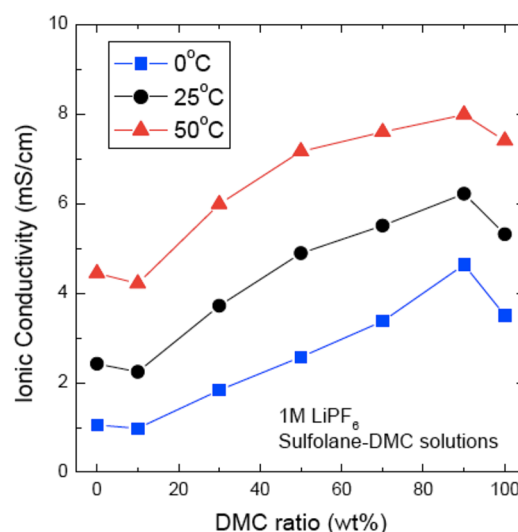
Figure 7. Conductivity isotherms for 1 M $LiPF_6$ in sulfolane−DMC mixtures showing weak increases, considerably below expectations from the corresponding viscosity decreases of Figure 6.

In Figure 8, this conductivity loss is quantified by the Walden plot. Except for the data for the EMS-FMS (1:1 solvent case),
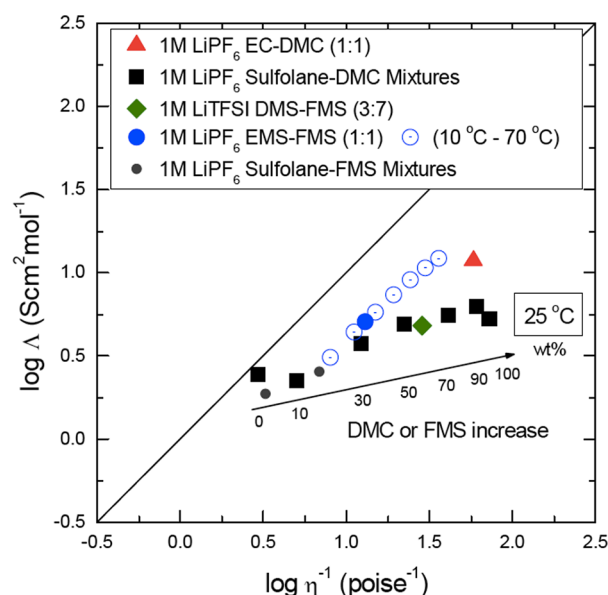
Figure 8. Walden plot for the key solutions of this paper. Most data are for single compositions at 25 °C. Filled triangle is for the standard electrolyte. Data confirm and extend the initial findings of Figure 2. Included are limited data for the all-sulfone system sulfolane + FMS, a single point for a 3:7 solution of DMS + FMS, and data for the 1:1 solution of EMS + FMS covering the temperature range 10−70 °C.

all data in Figure 8 are for 25 °C . The plot includes data for two 1 M $LiPF_6$ in sulfolane + FMS solutions and for one solution of LiTFSI in the simplest (high polarity but high-melting) sulfone (DMS) stabilized for low-temperature study by mixing (3:7) with FMS. The data and their implications are discussed below.

■ DISCUSSION

Our discussion of these findings starts with some consideration of the general problem of reaching high conductivities (hence

high power) with batteries utilizing nonaqueous solution electrolytes. The maximum ambient temperature *molar* conductivities that are realized, indicated by Figure 8 to be on the order 1 S cm^2 mol^{-1}, fall very far short of the theoretical limit of 10^4 S cm^2 mol^{-1} (indicated by extrapolation of high ionicity electrolyte Walden plots to the high fluidity limit of 10^4 (Pa·s)$^{-1}$ or by extrapolation of infinitely dilute aqueous solution data to infinite temperature). (See figure 3 of ref 20.) These limiting mobility measurements correspond in practical terms to maximum *specific* conductivity values of ~10 S cm^2, which is also the "infrared conductivity" of glassy ionic conductors.[21]

The reason for the 3 decade shortfall in conductivity is fundamentally due to the connection between solvent fluidity and solvent dipolarity, which translates to high fluidity solvents having poor ability to dissociate salts efficiently. Whereas water and aqueous solutions are always exceptional to this generalization, it seems that all nonaqueous solvents have the disadvantage that the solvents that combine the desired low volatility with high salt-dissociating power (i.e., with either high dielectric constants or high Lewis basicity) are always rather viscous.

The unfortunate correlation of fluidity with volatility, expected since Eyring's 1941 theory of viscosity and shown in Figure 9 for a wide selection of solvents, including some of
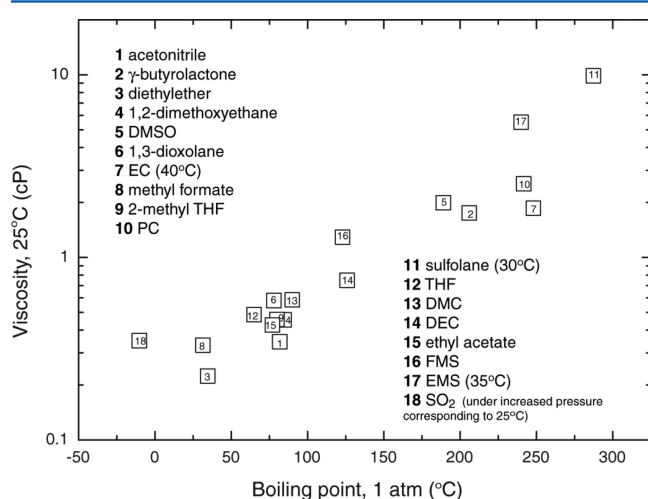

Figure 9. Correlation of involatility, indicated by normal (1 atm) boiling point, with viscosity at 25 °C (or at melting point in the case of sulfolane, EC, and EMS) for a wide range of solvents, showing the generality of the link between volatility and fluidity for molecular liquids.

the present study cases, seems to be of broad validity.[22−24] It is only seriously challenged by the case of ionic liquids. The latter would then seem to be ideal electrolyte solvents, but unfortunately there seem to be separate fundamental problems linked to intrinsic high viscosity (due to our inability to reduce the coulomb energy to low values without increasing the van der Waals energy excessively[2]) on the one hand and to supercoupling of any lithium cation that is dissolved therein[25] on the other hand. The *inorganic ionic liquids*, or corresponding plastic crystals, with weakly bound alkali cations needed to overcome these problems have yet to be developed, although their probable existence is hinted at by the reality of single-crystal β''alumina with ambient temperature conductivity of 100 mS cm^{-2}.[26]

Is there an alternative to the dipolar solvents that have dominated the field to this point? The existence of polymer electrolytes in which the alkali salts dissolve in a matrix of low dielectric constant ($\varepsilon = 3-5$) by interaction with polyether oxygens of high Lewis basicity suggests that there may be, and indeed Watanabe and coworkers[27] have recently shown that a chelated lithium cation salt, enabled by the basic oxygens in the oligoether tetraglyme, can function as an interesting (class 4) ionic liquid with strikingly good lithium battery performances.[28] Unfortunately, the lithium mobility remains restricted by the chelation, and high ionicity is guaranteed only in the presence of superacid (weak base) anions.[29]

Therefore, unless interactive supporting matrices for the molecular-solvent-based systems (Celgard is neutral) can be developed, there seems to be little alternative to the compromise that is being made in the adoption of the low ionicity (Figures 2 and 8) mixed liquid solvent systems that are currently in use. This applies equally to the problem of generating electrolyte solvents that can serve at low temperatures (down to −60 °C) for which ester cosolvents[30] seem to be useful.[31]

Cell studies to be reported separately[17] make it increasingly clear that once high conductivity is established the best combination of solvating and cosolvent components will be determined *not* only by dielectric properties or intrinisic redox stabilities but also by the (quite unrelated) ability of the total electrolyte-electrode system to form suitable SEIs.[32] We remark here that the SEI structures, so far discovered by serendipity, must be closely related to the alkali cation superionic phases being sought consciously in inorganic ionic liquid, superionic glass,[33−35] and ceramic[36,37] research programs.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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