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Conductivity and Viscosity of Solutions of $LiCF_3SO_3$, $Li(CF_3SO_2)_2N$, and Their Mixtures

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ABSTRACT

The high level of charge delocalization of the $Li(CF_3SO_2)_2N$ anion reduces ion pairing in nonaqueous electrolytes. This overrides the higher viscosity of the imide-containing solutions making the electrolytes much more conductive than those containing $LiCF_3SO_3$, especially in low dielectric ether-based solvent systems commonly used in secondary lithium batteries. In more viscous solvent systems (1:1 propylene carbonate:1,2-dimethoxyethane) or at low temperatures, the imide affords less of an advantage in conductivity due to the more important role of viscosity. The cyclic imide $\mathrm{Li}\underline{\mathrm{SO_2\text{-}(CF_2)_4\text{-}SO_2\text{-}N}}$ gives more viscous and less conductive solutions than does $Li(CF_3SO_2)_2N$. The degree of dissociation in 1:1 PC:DME appears to be

$$LiPF_6 \approx LiAsF_6 > LiClO_4 \approx Li(CF_3SO_2)_2N \approx \mathrm{Li}\underline{\mathrm{SO_2\text{-}(CF_2)_4\text{-}SO_2\text{-}N}} >> LiBF_4 >> LiCF_3SO_3$$

The number of lithium salts suitable for use in lithium high energy density batteries is rather limited. Generally most salts have been found to be either insoluble (most dianions, for example) or unstable to the lithium anode[1]. Of those reported, many have poor stability and/or undesirable safety characteristics, particularly those often used in secondary lithium systems. $LiClO_4$ can lead to explosions under certain conditions[2,3] and while $LiAsF_6$ is not in itself particularly toxic[4], there is considerable concern regarding both the effect of disposal of such cells on the environment and the toxicity of salt degradation products[5-8] which may be present in the cells. $LiBF_4$ and $LiPF_6$ have been used but are themselves not as stable as one would wish. $LiCF_3SO_3$ (lithium "triflate") is a more stable, safer salt which is commonly used in primary lithium cells. Its main disadvantage is the low conductivity of lithium triflate electrolytes.

Recently, the availability of the lithium imide salt $Li(CF_3SO_2)_2N$ (lithium bistrifluoromethylsulfonyl imide) has sparked considerable interest in the lithium battery field. This salt is reported to offer much greater conductivity than can be attained with the triflate salt[9] and yet the imide appears to have good stability[9] and safety characteristics. Thus, it would seem possible to use the imide salt to produce highly conductive electrolytes with stability and safety characteristics similar to those of triflate solutions. Such electrolytes could improve the characteristics of both primary and secondary lithium batteries.

Apart from some conductivity studies[9] reported by Koch *et al.*, very little conductivity and no viscosity data are available on nonaqueous electrolytes using the imide salt. Therefore, we measured conductivities of solutions containing $LiCF_3SO_3$, $Li(CF_3SO_2)_2N$, and their mixtures in two solvent systems at various temperatures and salt concentrations. We have also performed some more limited measurements on solutions containing a related cyclic imide (I) $\mathrm{Li}\underline{\mathrm{SO_2\text{-}(CF_2)_4\text{-}SO_2\text{-}N}}$.

Viscosity measurements have proved invaluable in helping us to understand how the interrelationship between the solvent properties (dielectric constant and viscosity) and the charge delocalization and size of the lithium salt anion affect electrolyte conductivity.

Experimental

All solutions were prepared in an argon-filled Vacuum Atmospheres HE-43 dry box equipped with an HE-493 DRI-TRAIN (moisture $_3SO_3$, $Li(CF_3SO_2)_2N$, and (I) were provided by 3M Corporation and were vacuum dried at 110°C in the antechamber of a dry box and transferred under argon. $LiClO_4$ (G.F. Smith Chemical Company) was vacuum dried at 160°C.

$LiAsF_6$ (Lithium Corporation of America) and $LiPF_6$ (Hashimoto Chemical Industrial Company) were used as received. Typical water levels of the electrolytes were 20-70 ppm (Karl-Fischer titration).

Conductivities were measured using Yellow Springs Instrument Company (YSI) 3403 probes and a YSI-34 conductivity meter. Samples were placed in glass, jacketed U tubes. The sample tubes were sealed in the dry box using standard ground glass "ACE-THRED" joints holding the conductivity cells. Each cell was platinized and cleaned at the beginning of this study and calibrated with an aqueous YSI 3161 conductivity standard at 25.0°C and again with 0.6735 *m* $LiClO_4$ in PC. This composition is close to that giving the maximum conductivity for $LiClO_4$ in PC and is used in our dry box as a convenient secondary standard. We use values calculated from the Casteel-Amis equation for $LiClO_4$/PC solutions reported by Barthel *et al.*[10] ($5.419 \times 10^{-3}\ W^{-1}\ cm^{-1}$ for 0.6735 *m* $LiClO_4$ in PC at 25°C). Our conductivity values agreed with those of Barthel *et al.* to within 1%.

For convenience, the samples were made up on the basis of moles of salt per liter of solvent, which we denote C_s. The molality of the samples can be calculated from the density of the solvent system (given in Table I). Molonities (mols salt/Kg solution) and molarities can then be calculated from equations given in Ref. (10) using the following relationships for the density (r) of the electrolytes

For $LiCF_3SO_3$ in 1:1 PC:DME	$r = 1.0481 + 0.0705C_s$
For $Li(CF_3SO_2)_2N$ in 1:1 PC:DME	$r = 1.0572 + 0.1102C_s$
For $LiCF_3SO_3$ in 5:4:1 DIOX:DME:PC	$r = 1.0074 + 0.0723C_s$
For $Li(CF_3SO_2)_2N$ in 5:4:1 DIOX:DME:PC	$r = 1.0125 + 0.1254C_s$

The densities of the samples were measured with a Paar DMA35 four-place density meter and the viscosities with Canon-Fenske viscometers placed in a Schott-Geräte tempering jacket. The temperature

Table I. Solvent systems used in this work.

Physical properties at 25°C	1:1 PC:DME	5:4:1 DIOX:DME:PC ("High Ether")
Density (g/ml)	1.0402	0.9993
Viscosity (cP)	1.00	0.59
Dielectric constant[a]	35.8	12.9

[a] Estimated from $e_{mix} = S\, y_i e_i$ where y_i is the volume fraction of the *i*th component. Note that these are very similar to the following related experimental values (12):
1:1 PC:DME at 20°C e = 40 (the above formula gives 41 at 20°C).
1:9 PC:DME at 25°C e = 13.16.

of the samples during the conductivity, viscosity, and density measurements were held to within 0.03°C of the set point with either Haake A81 or F-3 circulators. Viscosities and densities were measured under ambient humidity (moisture pick-up during these measurements should not significantly affect the accuracy of the results).

Results and Discussion

Since single-solvent systems have rarely been found suitable for use in lithium batteries, we concentrated our studies on two solvent blends of interest to us in our lithium battery development program. The first is a 1:1 by volume PC:DME mixture commonly used by many battery manufacturers. This mixture has a relatively high dielectric constant and moderate viscosity (Table I). The second is a proprietary[11] three solvent blend of 5:4:1 by volume DIOX:DME:PC. This blend, which we will denote the "high-ether" solvent blend, has a much lower viscosity and dielectric constant. Solvent blends with high levels of ethers such as these have been reported by various workers, particularly for secondary cells. Samples of triflate and the imide, $Li(CF_3SO_2)_2N$, were formulated with salt concentrations varying between 0.5 and 1.5 mols salt/liter solvent.

The much higher molecular weight of the imide, 287 *vs*. 156 for the triflate salt, necessitates the addition of larger amounts of salt for equimolar solutions. Depending on the type of battery, the salt used in the electrolyte can represent a significant portion of the cost of lithium batteries. This is particularly true of large, primary batteries for the general consumer market. The raw material costs become relatively less important for smaller batteries, such as coin cells, when the fabrication and general overhead costs are taken into account. Moreover, batteries for specialized applications (e.g., biomedical) or rechargeable batteries may be less price sensitive if the more expensive raw materials yield significant performance gains. In view of these cost considerations, we explored the effect of small additions of the imide on the conductivity of the triflate solutions, as well as a direct substitution. Solutions were made by mixing the individual equimolar $LiCF_3SO_3$ and imide solutions in various ratios to give 10:90, 20:80, 35:65, 50:50, and 75:25 imide:triflate mole ratios for each salt concentration. Volume changes during the blending process were ignored, and thus the total salt concentrations of the mixed salt electrolytes may differ slightly from that of the single salt solutions used to generate them.

It should be emphasized that the experiments described in this report are designed for characterizing the effect of salt type, concentration, and solvent blend on the conductivity of practical electrolytes for lithium cells. While the methods used are sufficiently accurate for this work, much more intricate methods would be necessary to determine fundamental properties of the salts such as the limiting equivalent conductivities and association constants. This is beyond the scope of this report.

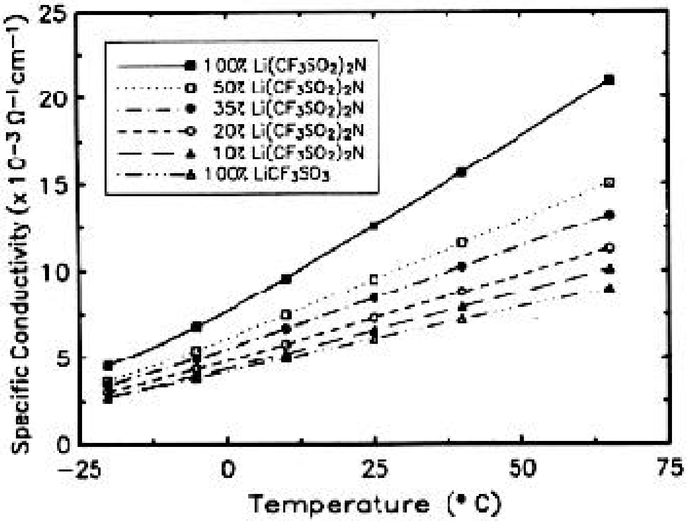


Fig. 1. Conductivity of $LiCF_3SO_3$ and $Li(CF_3SO_2)_2N$ mixed salt electrolytes in 1:1 PC:DME as a function of temperature. All samples are 1 mole salt/liter solvent.

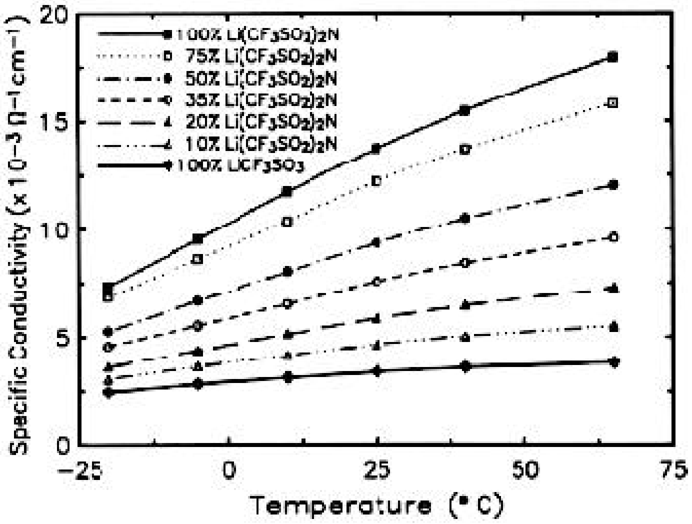
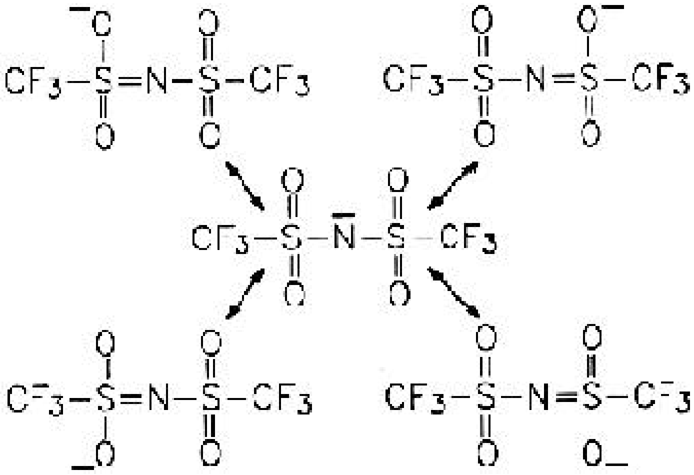


Fig. 2. Conductivity of $LiCF_3SO_3$ and $Li(CF_3SO_2)_2N$ mixed salt electrolytes in 5:4:1 DIOX:DME:PC as a function of temperature. All samples are 1 mole salt/liter solvent.

Our results reflect the interaction of the dielectric constant and viscosity of the solvent with the size and charge delocalization of the lithium salts. Figures 1 and 2 show how the conductivity of the one molar solutions varies with temperature in both solvent systems. Plots of the conductivities at other salt concentrations are essentially similar. The data reaffirm that solutions containing the imide salt are more conductive than the corresponding triflate solutions (at least under the conditions we have investigated). For example, linear regression analysis of the specific conductivity, k, of the one molar solutions at 25°C vs. mole percent (m/o) of the salt corresponding to the imide gives

$$k = 6.02 \times 10^{-3} + (7.03 \times 10^{-5} \times \%\ \text{imide})\ W^{-1}\ cm^{-1}$$
$$(r = 0.988,\ \text{standard error of predication} = 4.3 \times 10^{-4}\ W^{-1}\ cm^{-1})$$

This basically reflects the greater degree of dissociation which is afforded by the imide salt. The imide anion has much greater opportunities for charge delocalization than is available to the triflate anion. As shown below, all the sulfur, nitrogen, and oxygen atoms can participate in dispersing the charge on the imide anion, which promotes dissociation. The strong electron-withdrawing power of the terminal $-CF_3$ groups also helps to delocalize the anion's charge.



The viscosities of the imide electrolytes are greater than those of the corresponding triflate solutions for both solvent systems (Fig. 3). This is due to the larger size of the imide salt and tends to offset the effect of the greater degree of dissociation of the imide salt. The viscosities of the PC:DME electrolytes are greater than those of the high-ether solutions, reflecting the viscosity of the solvent systems. The viscosities of these solutions exhibit normal Arrhenius behavior (Fig. 4).

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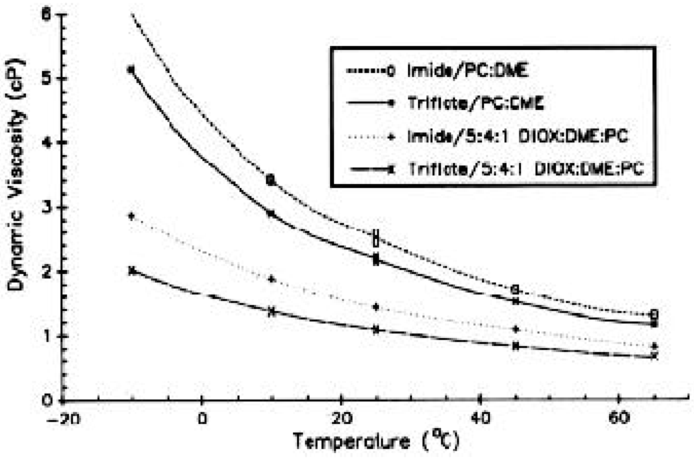

Fig. 3. Viscosity of $LiCF_3SO_3$ and $Li(CF_3SO_2)_2N$ in 1:1 PC:DME and 5:4:1 DIOX:DME:PC as a function of temperature. All samples are 1 mole salt/liter solvent.

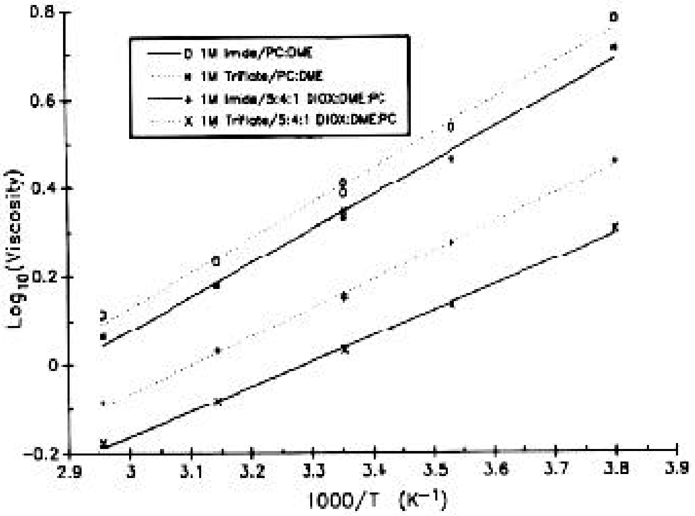

Fig. 4. Arrhenius plot of log10 viscosity of $LiCF_3SO_3$ and $Li(CF_3SO_2)_2N$ electrolytes in 1:1 PC:DME and 5:4:1 DIOX:DME:PC vs. the inverse of the absolute temperature. All samples are 1 mole salt/liter solvent.

The conductivity advantage afforded by the imide salt is greater in the high-ether solvent system (Fig. 5). Linear regression analysis of the specific conductivity of the one molar solutions at 25°C vs. m/o of the salt corresponding to the imide gives

$$k = 3.70 \times 10^{-3} + (1.06 \times 10^{-4} \times \%\ \text{imide})\ W^{-1}\ cm^{-1}$$
$$(r = 0.995,\ \text{standard error of predication} = 4.2 \times 10^{-4}\ W^{-1}\ cm^{-1})$$

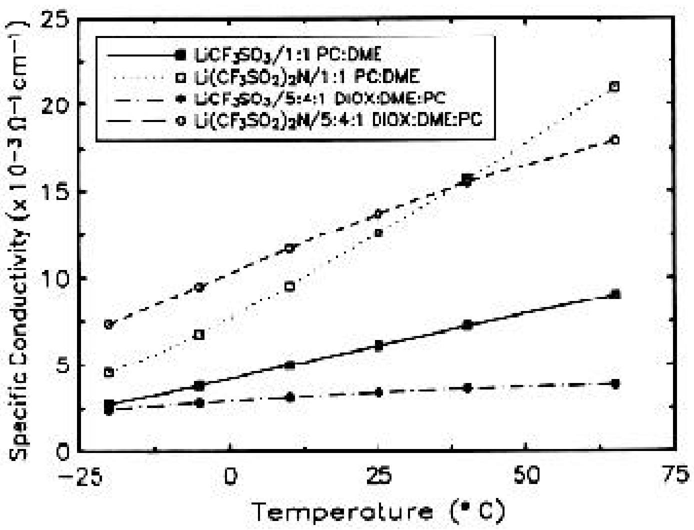

Fig. 5. Conductivity of $LiCF_3SO_3$ and $Li(CF_3SO_2)_2N$ in 1:1 PC:DME and 5:4:1 DIOX:DME:PC as a function of temperature. All samples are 1 mole salt/liter solvent.

Table II. Conductivities of various salts in both solvent systems.

Salt	1:1 PC:DME (x 10^{-3} W^{-1} cm^{-1})	5:4:1 DIOX:DME:PC (x 10^{-3} W^{-1} cm^{-1})
$LiCF_3SO_3$	6.2	3.4
$Li(CF_3SO_2)_2N$	12.5	14.0
$LiClO_4$	13.7	10.3
$LiAsF_6$	14.8	11.8

All solutions are 1 mol/liter solvent. Measurements made at 25°C.

This is because of two factors. The low viscosity of this solvent blend means that the effect of the higher viscosity of the imide samples is not as important as in the PC:DME solutions, where viscosity plays a more important role in limiting the conductivity of the electrolyte. In addition, the lower dielectric constant of the high-ether solvent system results in a greater degree of ion pairing. Thus, the conductivity in the high-ether solvent blend is more sensitive to the charge density of the salt anion than are the higher dielectric PC:DME solutions. In fact, this is the only lithium salt we have found where the conductivity of a one molar solution (at 25°C) is greater in the high-ether blend than in PC:DME (Table II). Similarly, in some limited studies we have found that the conductivity of the imide solutions in PC:DME increases if the PC content is lowered slightly.

Our results show that the improvement in conductivity afforded by the imide salt diminishes as the temperature becomes lower (Fig. 1 and 2). This can be explained by considering the effect of temperature on the viscosity and dielectric properties of the solutions. At low temperatures the viscosity of the electrolytes increases, as should their dielectric constant. The increase in dielectric constant slightly reduces the extent of ion pairing in the electrolytes. However, this is overridden by the increase in viscosity which becomes much more important in limiting the conductivity of the electrolyte. Consequently, at low temperature the higher viscosity of the imide-containing electrolytes becomes much more of a liability and the higher degree of association which occurs with the triflate salt is somewhat alleviated by the increase in dielectric constant. Both these factors tend to reduce the conductivity advantage of the imide salt over lithium triflate at lower temperatures. The difference in conductivity between solutions containing the two salts at low temperature is smaller in the more viscous PC:DME solvent system than for the high-ether samples. Again, this illustrates the increasingly important role of viscosity at low temperature.

To better reveal the effect of viscosity and ion pairing on the electrolyte conductivity we plot the product of specific conductivity and viscosity, similar to a Walden product, for those samples having a concentration of 1 mole salt/liter solvent in Fig. 6. We have found these values to be a very helpful albeit somewhat crude way to understand the roles of viscosity and association in determining electrolyte conductivity, even though the highly associated nature of some of these electrolytes makes

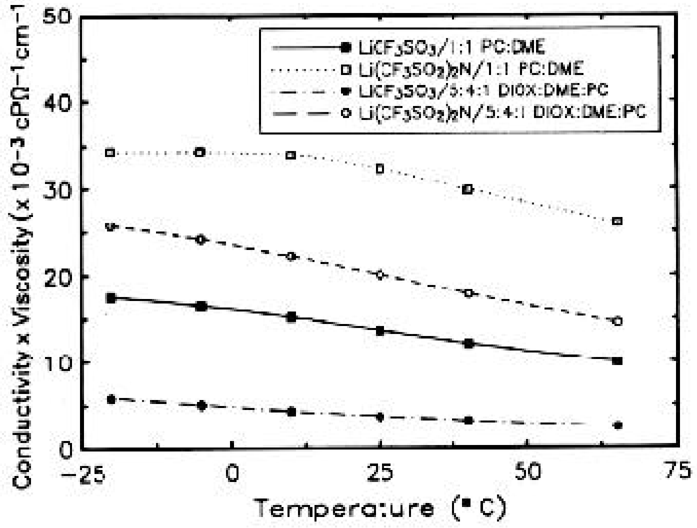

Fig. 6. Conductivity x viscosity of $LiCF_3SO_3$ and $Li(CF_3SO_2)_2N$ in 1:1 PC:DME and 5:4:1 DIOX:DME:PC as a function of temperature. All samples are 1 mole salt/liter solvent.

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Table III. Densities, conductivities, viscosities, and Walden products of various lithium salts in 1:1 PC:DME at 25°C.

Salt	Viscosity (cP)	Specific conductivity $(x\ 10^{-3}\ W^{-1}\ cm^{-1})$	Walden product $(x\ 10^{-3}\ cPW^{-1}\ cm^{-1})$
$LiBF_4$	1.99	9.46	18.9
$LiCF_3SO_3$	2.22	6.12	13.6
$Li(CF_3SO_2)_2N$	2.55	12.6	32.1
$\mathrm{Li}\underline{\mathrm{SO_2\text{-}(CF_2)_4\text{-}SO_2\text{-}N}}$	3.14	10.2	32.1
$LiClO_4$	2.32	13.5	31.4
$LiAsF_6$	2.61	14.8	38.6
$LiPF_6$	2.54	15.3	38.8

All solutions are 1 mol/liter solvent.

comparisons between different solvent systems difficult. The higher values for the PC:DME samples and for the imide-containing electolytes confirm that ion pairing is less prevalent under these conditions. The values for all the electrolytes slightly increase as the temperature is lowered, presumably reflecting the increase in dielectric constant. The increase in dielectric constant would have a relatively greater effect in the high-ether solvent blend than in the PC:DME mixture, which already possesses good dielectric properties.

Figures 7 and 8 show the effect of salt concentration on conductivity at 25°C for the PC:DME and the high-ether samples. The conductivity maxima generally fall around 1.1 mols/liter solvent for the PC:DME electrolytes. The conductivity maxima shift to slightly lower concentrations at low temperature, as the higher viscosity of the concentrated solutions becomes more detrimental to conductivity. Similarly, increasing amounts of the imide salt in the sample increases th electrolyte's viscosity. This also causes the conductivity maximum to move to lower salt concentrations where the higher viscosity of the imide solutions becomes less detrimental. The conductivity maxima for the high-ether electrolytes are somewhat higher, generally around 1.2-1.5 mols/liter solvent. Again, this is because the higher viscosity of the more concentrated samples has less of an effect on the conductivity than in the more viscous PC:DME solutions.

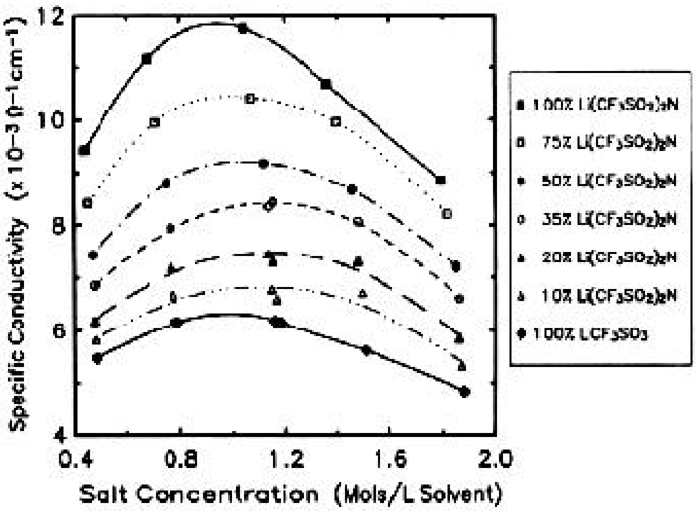

Fig. 7. Conductivitiy of $LiCF_3SO_3$ and $Li(CF_3SO_2)_2N$ in 1:1 PC:DME as a function of concentration at 25°C.

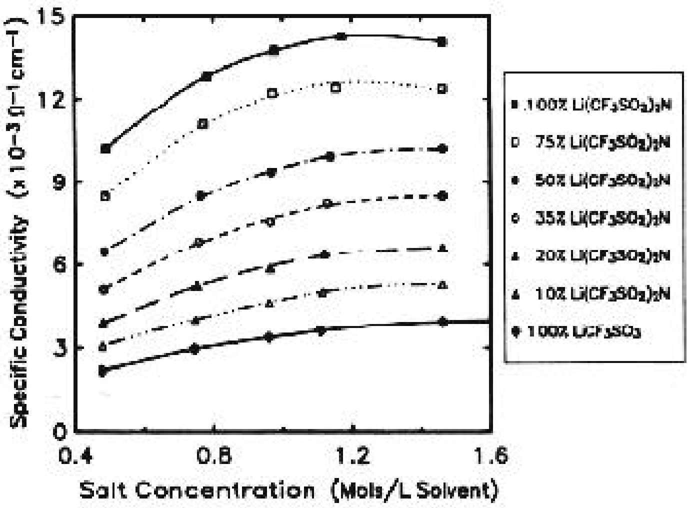

Fig. 8. Conductivity of $LiCF_3SO_3$ and $Li(CF_3SO_2)_2N$ in 5:4:1 DIOX:DME:PC as a function of concentration at 25°C.

Cyclic imide (I).—Finally, we performed a limited study on the cyclic imide[1] (I) in both solvent systems. Samples containing this salt essentially behave similarly to those containing the linear imide, $Li(CF_3SO_2)_2N$. The viscosity of samples containing (I) are greater than those containing the linear imide (Fig. 9) and consequently the conductivities are lower. Again, the effect of the higher viscosity is more important for the more viscous PC:DME electrolytes.

Comparison with other salts.—The densities, viscosities, conductivities, and Walden products of other lithium salts in 1:1 PC:DME were also measured at 25°C (Table III). Comparison of the Walden products suggests that the imide salts are probably dissociated as highly as $LiClO_4$ under these conditions, but not quite as much as are $LiPF_6$ or $LiAsF_6$. Overall, the degree of dissociation in 1:1 PC:DME appears to be as follows

$$LiPF_6 \approx LiAsF_6 > LiClO_4 \approx Li(CF_3SO_2)_2N$$
$$\approx \mathrm{Li}\underline{\mathrm{SO_2\text{-}(CF_2)_4\text{-}SO_2\text{-}N}} >> LiBF_4 >> LiCF_3SO_3$$

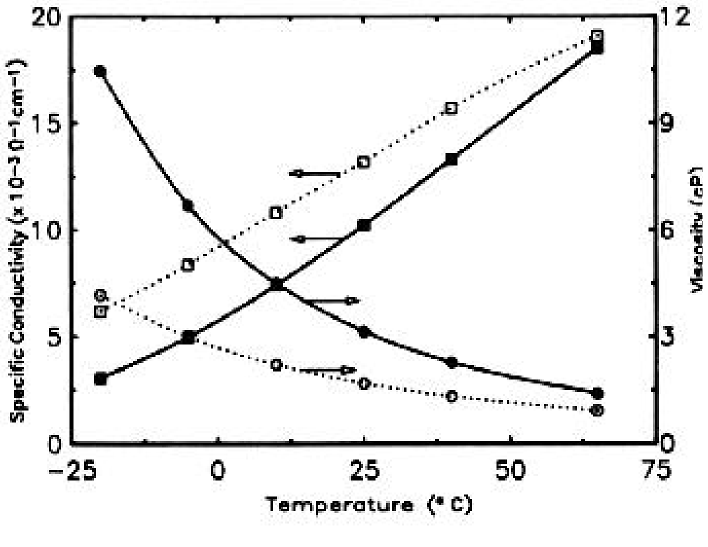

Fig. 9. Conductivity and viscosity of (I) in 1:1 PC:DME (solid lines) and 5:4:1 DIOX:DME:PC (dotted lines) as a function of temperature. Both samples are 1 mole salt/liter solvent.

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[1] Warning: The cyclic imide (I) has been found to be highly toxic in both oral ingestion and skin absorption tests on laboratory animals.

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Summary and Conclusions

The high level of charge delocalization of the imide anions reduces ion pairing in these electrolytes and so conductivities are higher than can be obtained with the triflate salt, despite the higher viscosities associated with the larger imide anions. The improvement in conductivity afforded by the imide salts is greatest in low-dielectric (high-ether) media of the type commonly used in secondary lithium batteries. With more viscous solvent systems or at low temperatures the imides show less of an advantage due to the more important role of viscosity in determining the conductivity of such samples. In our studies the cyclic imide (I) gives slightly more viscous and less conductive solutions than the linear imide, $Li(CF_3SO_2)_2N$.

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