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Conductivities and Electrochemical Stabilities of Lithium Salts of Polyfluoroalkoxyaluminate Superweak Anions

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Six lithium salts of tris- and tetrakis(polyfluoroalkoxy)aluminate superweak anions have been studied for their potential use as battery electrolytes. Four of the six are based on the formula $LiAl(OCR(CF_3)_2)_4$ (R = H, Me, CF_3, Ph); the other two are $LiAl(OCH_2CF_3)_4$ and $LiAlF(OCPh(CF_3)_2)_3$. The thermally stable electrolytes $LiAl(OCH(CF_3)_2)_4$ and $LiAl(OCPh(CF_3)_2)_4$ were not oxidized at potentials less than or equal to 5.0 V *vs.* $Li^{+/0}$ in dimethoxyethane (DME) or in 50:50% ethylene carbonate:dimethylcarbonate (EC:DMC). The $LiAl(OCH(CF_3)_2)_4$ electrolyte was not reduced at 0 V *vs.* $Li^{+/0}$ in DME. Neither $LiAl(OCH(CF_3)_2)_4$ nor $LiAl(OCPh(CF_3)_2)_4$ promoted the corrosion of aluminum at 5.0 V *vs.* $Li^{+/0}$. The electrolyte $LiAl(OCH(CF_3)_2)_4$ underwent efficient, reversible reductive intercalation of Li^+ with MCMB carbon or $LiCoO_2$ electrodes over the potential ranges 0-2 and 2.4-4.8 V, respectively, *vs.* $Li^{+/0}$, but did not react in any other way with these electrode materials. The conductivities of some of the $LiAl(OR_F)_4$ electrolytes in DME or in EC:DMC were high enough for them to be considered as potential replacements for $LiPF_6$ in primary and secondary lithium batteries.

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We recently reported the conductivity and electrochemical behavior of lithium salts of new bis(polyfluorodiolato)borates such as $B(OC(2\text{-}O\text{-}C_6H_4)(CF_3)_2)_2^-$.[1] These salts satisfied a number of requirements as potential replacements for $LiPF_6$ in nonaqueous primary and secondary lithium batteries.[2-5] As far as electrolytes are concerned, suitable lithium salts must be (*i*) readily available at a reasonable cost, (*ii*) highly conductive in solution ($\geqslant 5$ mS cm^{-1}), (*iii*) thermally more stable than $LiPF_6$, which decomposes at temperatures well below 100°C in the solid state and in solution,[6,7] (*iv*) electrochemically stable in a suitable solvent when in contact with commonly used anodes and cathodes, and (*v*) must not cause significant corrosion of aluminum current collectors at high positive potentials.

In this paper we report a parallel study of six lithium salts of polyfluoroalkoxyaluminates. We[8-12] and others[13] have reported the synthesis and properties of a series of lithium salts of superweak (*i.e.*, extremely weakly coordinating[14-17]) tetrakis(polyfluoroalkoxy) aluminate anions. The first example, $LiAl(OC(Ph)(CF_3)_2)_4(LiAl(HFPP)_4)$, was reported by us in 1996.[12] One of the salts we previously synthesized, $LiAl(OCH(CF_3)_2)_4(LiAl(HFIP)_4)$,[8] has recently been studied as a component of a nano-composite electrolyte.[18]

Experimental

Materials.—All syntheses, manipulations, and measurements were done under an inert atmosphere of purified argon or helium using Schlenk, glovebox, or high-vacuum techniques.[19] Battery grade dimethoxyethane (DME), ethylene carbonate (EC), propylene carbonate (PC), and dimethyl carbonate (DMC) were stored in a glovebox and used as received from Mitsubishi Chemical. The fluoroalcohols $HOCH_2CF_3$ (H(TFE), Aldrich) and $HOCPh(CF_3)_2$ (H(HFPP), Central Glass) were dried with 4 Å molecular sieves. The compounds $LiAlH_4$ (Aldrich) and $LiPF_6$ (Central Glass) were used as received. MCMB carbon (Osaka Gas Chemicals) and $LiCoO_2$ (Nippon Chemical) were used as received. The electrolytes $LiAl(HFIP)_4$,[8] $LiAl(OC(CH_3)(CF_3)_2)_4$ $(LiAl(HFTB)_4)$,[10,13] $LiAl(HFPP)_4$,[12] and $LiAl(OC(CF_3)_3)_4$ $(LiAl(PFTB)_4)$[10,13] were prepared as described in the literature.

LiAlF(HFPP)₃.—To a solution of H(HFPP) (70.0 g, 287 mmol) in toluene (150 mL) was added $LiAlH_4$ (2.7 g, 71.1 mmol) at room temperature. This mixture was stirred under reflux for 4 h. Heat was removed, and crystals formed upon cooling to room temperature. These were isolated by filtration and washed with hexane. Toluene (600 mL) was then added, the resulting suspension filtered, and the filtrate cooled to −40°C. The crystals that formed were collected by filtration and dried under vacuum to yield $LiAlF(HFPP)_3$ as a white powder. Yield 13.1 g (24% based on $LiAlH_4$). ^1H NMR (C_6D_6) δ 7.68 (m, 6 H), 7.06 (m, 9 H). ^{19}F NMR (C_6D_6) δ −75.9 (s). The fluorine atom attached to the aluminum atom was not observed in the ^{19}F NMR spectrum, presumably because of quadrupolar broadening by ^{27}Al. Low resolution mass spectrum (negative ion electrospray, CH_3CN solution) *m/z* 774.9 ($(M\text{-}Li)^-$; calcd. for $C_{27}H_{15}AlF_{19}O_3^-$, *m/z* 775.0).

LiAl(TFE)₄ · 0.1DME.—The fluoroalcohol H(TFE) (1.6 kg, 16 mol) was added with stirring to $LiAlH_4$ (38 g, 1 mol) at room temperature. The exothermic reaction heated the reaction mixture to 80°C. After 6 h of stirring, all volatiles were removed under vacuum, leaving a white solid. The solid was dissolved in DME, forming a cloudy mixture which was filtered to remove insoluble material. The solvent was removed from the clear, colorless filtrate under vacuum, and the white solid that remained was dried under vacuum at 60°C for 24 h. Yield 440 g (81% based on $LiAlH_4$). ^1H NMR (CD_3CN) δ 3.98 (s, 8 H), 3.30 (s, OCH_3), 3.46 (s, OCH_2). ^{19}F NMR (CD_3CN) δ −76.9 (s). The ^1H NMR spectrum demonstrated that the Li:DME molar ratio was 10:1.

Apparatus and measurements.—NMR spectra were recorded using a JEOL AL-400 spectrometer. DSC measurements were made using a Rigaku DSC8230 (20°C min^{-1} heating rate). Electrolytic conductivities were measured in an argon- or helium-filled glovebox at 24 ± 1°C using either a Kyoto Electronics Model K-111 conductivity cell ($k = 0.9878$ cm^{-1}) and a Kyoto Electronics Model CM-115 conductivity bridge operated at 1.2 KHz or a YSI Model 3403 conductivity cell ($k = 0.9988$ cm^{-1}) and a YSI model 32 conductivity bridge operated at 1 KHz. Measurements for the same compounds taken in Japan and in Fort Collins agreed to within experimental error, which were generally ±2%. All of the lithium salts were anhydrous as determined by ^1H NMR spectroscopy. Solutions of them were prepared in volumetric flasks in the glovebox. Although fixed-frequency conductivity measurements may differ by as

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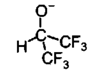
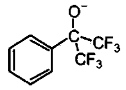
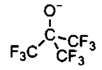
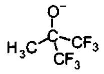
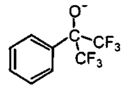
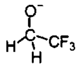
Table I. Thermal and electochemical stabilities and maximum conductivities of $LiPF_6$ and $LiAlF_u(OR_F)_{4-n}$ electrolytes[a].

Compound abbreviation alkoxide structure	Thermal decomposition temperature	E_{ox} (solvent, conc.) (V *vs.* $Li^{+/0}$)	σ_{max} (solvent, conc.) ($mS\ cm^{-1}$)	E_{max} for negligible aluminum corrosion (EC:DMC, V *vs.* $Li^{+/0}$)[b]
$LiPF_6$	40°C (solid)[c] 70°C (EC:DMC)	>5.0 (EC:DMC, 1.0 M)	*5.3 (DME, 0.3 M)*[d] *3.0 (DME, 0.2 M)*[d] *1.3 (DME, 0.1 M)*[d] 11.5 (EC:DMC, 1 M) 5.8 (PC, 1 M)	>5.0 V
$LiAl(OCH(CF_3)_2)_4$ $LiAl(HFIP)_4$ 	100°C (solid) >100°C (EC:DMC)	>5.2 (DME, 0.1 M) >5.0 (EC:DMC, 0.5 M)	11.2 (DME, 0.5 M) *6.2 (DME, 0.2 M)*[d] *3.2 (DME, 0.1 M)*[d] 6.3 (EC:DMC, 0.6 M) 3.4 (PC, 0.6 M)	>5.0 V
$LiAl(OCPh(CF_3)_2)_4$ $LiAl(HFPP)_4$ 	100°C (solid) >100°C (EC:DMC)	>5.2 (DME, 0.1 M) >5.0 (EC:DMC, 0.3 M)	4.2 (DME, 0.3 M) *3.5 (DME, 0.2 M)*[d] *2.1 (DME, 0.1 M)*[d] 3.2 (EC:DMC, 0.3 M)	>5.0 V
$LiAl(OC(CF_3)_3)_4$ $LiAl(PFTB)_4$ 			*6.4 (DME, 0.2 M)*[d] *3.6 (DME, 0.1 M)*[d]	
$LiAl(OC(CH_3)(CF_3)_2)_4$ $LiAl(HFTB)_4$ 			9.6 (DME, 0.5 M) *6.2 (DME, 0.2 M)*[d] *3.4 (DME, 0.1 M)*[d]	
$LiAlF(OCPh(CF_3)_2)_3$ $LiAlF(HFPP)_3$ 	>80°C (solid)		2.6 (DME, 0.5 M) *1.3 (DME, 0.2 M)*[d] *0.5 (DME, 0.1 M)*[d]	
$LiAl(OCH_2CF_3)_4$ $LiAl(TFE)_4$ 	>60°C (solid)		5.4 (DME, 0.8 M) *1.6 (DME, 0.2 M)*[d] *0.6 (DME, 0.1 M)*[d]	

[a] All data from this work unless otherwise noted. Abbreviations: HFIP = $OCH(CF_3)_2$; HFTB = $OC(CH_3)(CF_3)_2$; HFPP = $OCPh(CF_3)_2$; PFTB = $OC(CF_3)_3$; TFE = OCH_2CF_3; DME, 1,2-dimethoxyethane; EC:DMC, 50:50 mol % ethylene carbonate:dimethylcarbonate; PC, 1,2-propylene carbonate; E_{ox}, potential at which the aluminate anion is oxidized in the indicated solvent; σ_{max}, maximum conductivity in the solvent and at the concentration (conc.) indicated in parentheses.

[b] Duration of experiment was 1 h.

[c] From Ref. 6.

[d] The conductivity values in italics do not represent maximum conductivities.

much as 10% from variable-frequency complex impedance measurements, the relative conductivities of the new salts, an important issue in this work, differ by as much as four times the lowest value. Voltammetric and chronoamperometric experiments were performed at 24 ± 1°C in the glovebox using an ALS Model 600 electrochemical analyzer. The glassy carbon working electrode ($0.008\ cm^2$) was polished with alumina, rinsed and sonicated with distilled water, and dried before each use. The aluminum working electrodes (99.997%, $2.0\ cm^2$) were cleaned and dried before use. A new aluminum electrode was used for each experiment. The counter and reference electrodes were lithium foil (Honjo Chemical, 99.9%). The MCMB carbon anode was prepared by coating a drying an *N*-methylpyrolidone (NMP) paste containing the MCMB carbon (95 wt %) and polyvinylidene fluoride (PVDF, 5 wt %) on copper foil. The $LiCoO_2$ cathode was prepared by coating and drying an NMP paste containing $LiCoO_2$ (85 wt %) and PVDF (15 wt %) on aluminum foil. All voltammetric experiments were performed at a scan rate of $10\ mV\ s^{-1}$.

Results and Discussion

Minimum thermal stabilities.—Table I lists the formulas, abbreviations, and structures of the six electrolytes we have studied. In addition, our results for $LiPF_6$ have been added for comparison. DSC experiments revealed that two of the aluminate salts, $LiAl(HFIP)_4$ and $LiAl(HFPP)_4$, undergo thermal decomposition at 100°C, significantly higher than the 40°C thermal decomposition point of solid $LiPF_6$.[6] In addition, when ethylene carbonate:dimethyl carbonate (EC:DMC) solutions of these two lithium aluminates were heated to 100°C for 1 day, the room temperature conductivities, ^{19}F NMR spectra, and appearance (colorless solutions) was unchanged. Solutions of $LiPF_6$ in EC:DMC are reported to decompose at 85°C.[7] We found that an EC:DMC solution of $LiPF_6$ decomposed when heated to only 70°C for 1 day (the evidence for decomposition was a color change and the formation of a precipitate). We did not investigate the thermal stabilities of the other lithium aluminate salts listed in Table I.

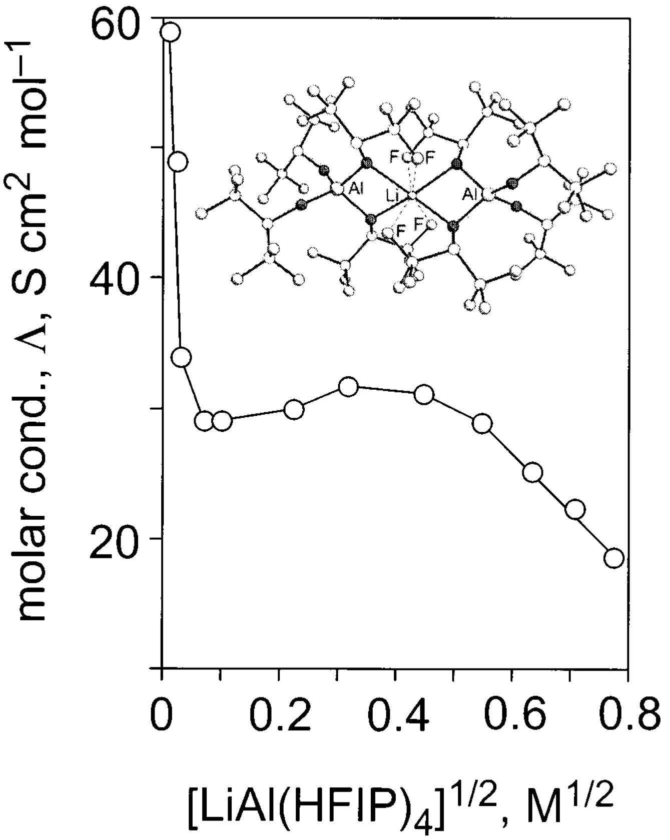


Figure 1. Molar conductivity *vs.* the square root of the concentration for DME solutions of $LiAl(HFIP)_4$ ($HFIP^- = OCH(CF_3)_2^-$). The lines drawn through the data points are a visual aid. The molecular species shown is the $[Al(HFIP)_4\text{-}Li\text{-}Al(HFIP)_4]^-$ triple ion in the structure of $[1\text{-}Et\text{-}3\text{-}Me\text{-}1,3\text{-}C_3H_3N_2][Li(Al(HFIP)_4)_2]$ (redrawn from Ref. 8). The unlabeled shaded gray spheres are oxygen atoms. The unlabeled unshaded and shaded white spheres represent carbon and fluorine atoms, respectively.

Conductivities.—The DME σ_{max} values for the six lithium aluminate electrolytes and for $LiPF_6$ are listed in Table I, along with 50:50 mol % EC:DMC σ_{max} values for $LiAl(HFIP)_4$, $LiAl(HFPP)_4$ and $LiPF_6$, and PC σ_{max} values for $LiAl(HFIP)_4$ and $LiPF_6$. Also listed are 0.1 and 0.2 M DME σ values for the seven electrolytes.

Figures 1 and 2 display plots of molar conductivity (Λ) *vs.* the square root of the concentration for DME solutions of $LiAl(HFIP)_4$, $LiAl(HFPP)_4$, and $LiAl(HFTB)_4$. A similar plot (not shown) was obtained for $LiAl(PFTB)_4$. The shape of the plots for $LiAl(HFIP)_4$ and $LiAl(HFTB)_4$, with a local minimum in Λ at *ca.* 0.01 M and a local maximum in Λ at *ca.* 0.1 M, is common for electrolytes in low-dielectric solvents (a similar curve for $LiBF_4$ in DME has been reported[20]) and has been interpreted in terms of significant triple-ion formation at concentrations above the local minimum.[21] The X-ray structure of the $Li(Al(HFIP)_4)_2^-$ inner-sphere triple ion[8] is reproduced in Fig. 1. The Li^+ ion is coordinated to two polyfluoroalkoxide oxygen atoms from each of the two $Al(HFIP)_4^-$ anions. The plot in Fig. 2 for $LiAl(HFPP)_4$ does not have a distinct local minimum and maximum. Nevertheless, the shape of the plot suggests that triple ions are also formed in DME solutions of this electrolyte. The lack of a local maximum for $LiAl(HFPP)_4$ suggests that the concentration of $Li(Al(HFPP))_4)_2^-$ inner-sphere triple ions in DME may be lower than for the other two lithium aluminate electrolytes. This may be due to steric hindrance of the bulky phenyl groups in the $Al(HFPP)_4^-$ anion. In support of this hypothesis, we note that the solid state structure of $LiAl(HFPP)_4$ is monomeric,[12] in contrast to the dimeric structure of $LiAl(HFIP)_4$, in which the $Al(HFIP)_4^-$ anions bridge the two Li^+ ions.[8]

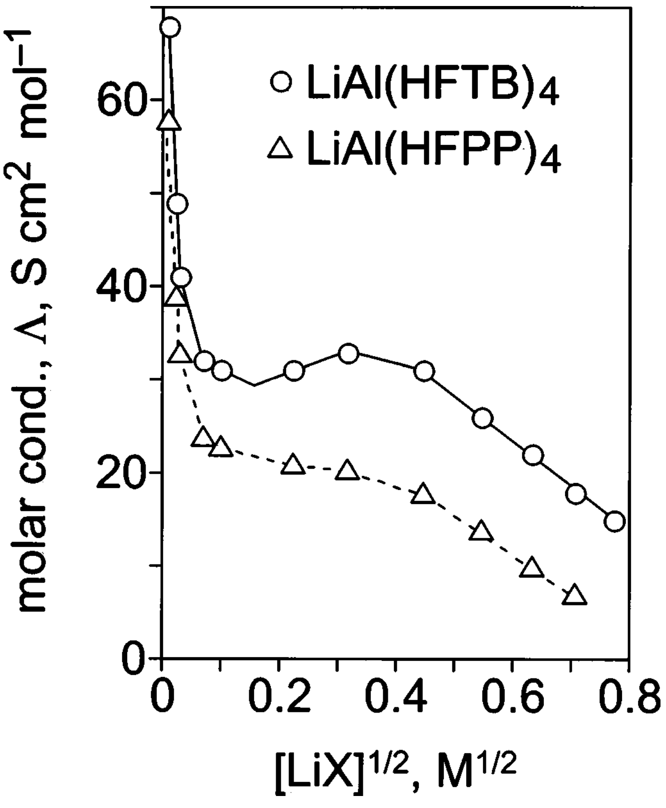


Figure 2. Molar conductivity *vs.* the square root of the concentration for DME solutions of $LiAl(HFTB)_4$ and $LiAl(HFPP)_4$ ($HFTB^- = OC(CH_3)\ (CF_3)_2^-$; $HFPP^- = OC(C_6H_5)(CF_3)_2^-$). The lines drawn through the data points are a visual aid.

The conductivity of a lithium salt of a molecular anion in a given solvent is dependent, to varying degrees at different concentrations, on (*i*) the coordinating and/or ion-pairing ability of the anion and (*ii*) the mobility of the anion, which in turn is closely correlated with the size of the anion. Figure 3 shows σ *vs.* DME concentration curves for five of the six lithium aluminate electrolytes in this study. The 0.1 and 0.2 M DME σ values for $LiAl(PFTB)_4$, which are not shown, are virtually the same as the corresponding σ values for $LiAl(HFIP)_4$ and $LiAl(HFTB)_4$ (see Table I). Solutions of $LiAl(PFTB)_4$ in DME more concentrated than 0.2 M could not be prepared because of the limited solubility of this perfluorinated electrolyte. It is significant that the σ values for $LiAl(HFPP)_4$ are lower at all concentrations than the corresponding σ values for $LiAl(HFIP)_4$, $LiAl(HFTB)_4$, or $LiAl(PFTB)_4$. Since all four anions are very weakly coordinating,[8] we do not think that differences in anion basicity or ion-pairing ability are responsible for the difference in σ values. We propose that the difference is due to the significantly larger size, and hence significantly increased solution viscosity and concomitant decreased mobility, of the $Al(HFPP)_4^-$ anion relative to the other three $Al(OCR(CF_3)_2)_4^-$ anions (R = H, CH_3, CF_3). This is consistent with the fact that σ_{max} occurs at only 0.3 M for $LiAl(HFPP)_4$ instead of at 0.5 M for $LiAl(HFIP)_4$ and $LiAl(HFTB)_4$. It is also consistent with the observation that σ_{max} for $LiAl(HFIP)_4$ is 17% higher than σ_{max} for $LiAl(HFTB)_4$, which contains the (slightly) larger anion. Not surprisingly, anion mobility does not affect σ as much at low concentrations as it does at high concentrations: the 0.05 M DME σ values of $LiAl(HFIP)_4$, $LiAl(HFTB)_4$, and $LiAl(HFPP)_4$ are very similar because their ion-pairing abilities (as well as their basicities[8]), are very similar.

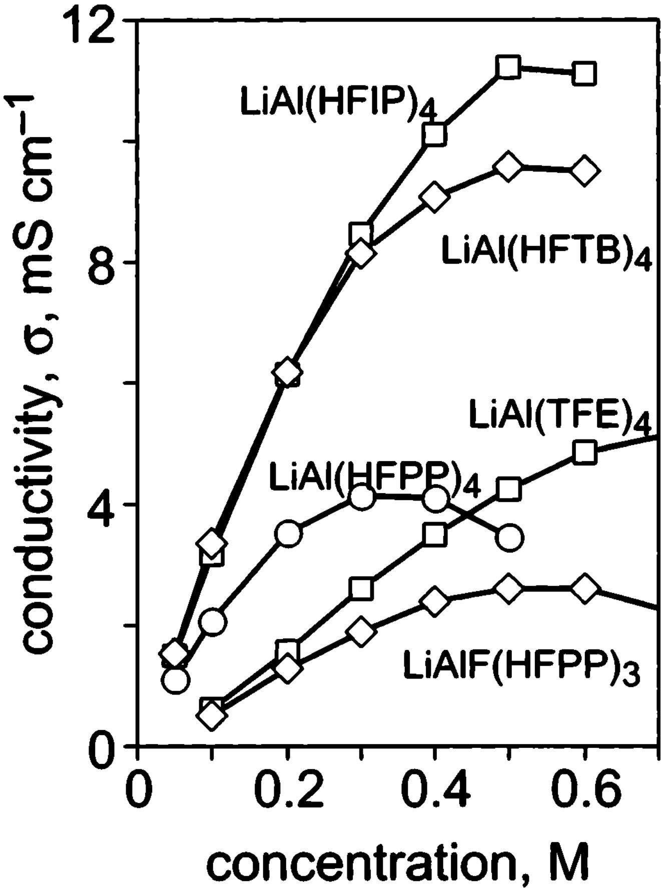


Figure 3. Conductivities of DME solutions of $LiAl(HFIP)_4$, $LiAl(HFTB)_4$, $LiAl(HFPP)_4$, $LiAl(TFE)_4$, and $LiAlF(HFPP)_3$ (HFIP $= OCH(CF_3)_2$; HFTB $= OC(CH_3)(CF_3)_2$; HFPP $= OCPh(CF_3)_2$; TFE $= OCH_2CF_3$).

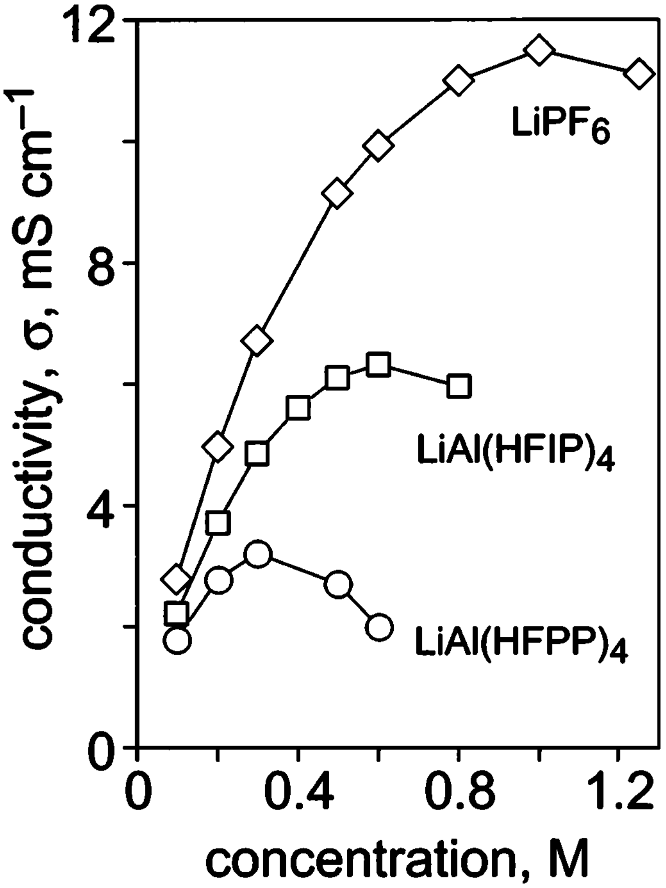


Figure 5. Conductivities of 50:50 mol % EC:DMC solutions of $LiAl(HFIP)_4$, $LiAl(HFPP)_4$, and $LiPF_6$ (HFIP $= OCH(CF_3)_2$; HFPP $= OCPh(CF_3)_2$).

However, the $LiAl(TFE)_4$ electrolyte, which contains the smallest of the five tetrakis(polyfluoroalkoxy)aluminates, also has the lowest DME σ values at 0.1 to 0.4 M. The anion in this electrolyte is electronically and sterically different than the four $Al(OCR(CF_3)_2)_4^-$ anions (R = H, CH_3, CF_3, Ph). It has only one CF_3 group per alkoxide substituent and is the smallest of the five $Al(OR_F)_4^-$ anions. For both of these reasons, we conclude that the $Al(TFE)_4^-$ anion is ion-paired with Li^+ to a much greater extent than are the four $Al(OCR(CF_3)_2)_4^-$ anions, leading to the relatively low σ values. On the other hand, the small size of the $Al(TFE)_4^-$ anion is responsible for the fact that σ continues to increase at concentrations between 0.5 and 0.8 M, presumably because the viscosity of a 0.5 M DME solution of $LiAl(TFE)_4$ is lower than the viscosity of a 0.5 M DME solution of either $LiAl(HFIP)_4$ or $LiAl(HFTB)_4$.

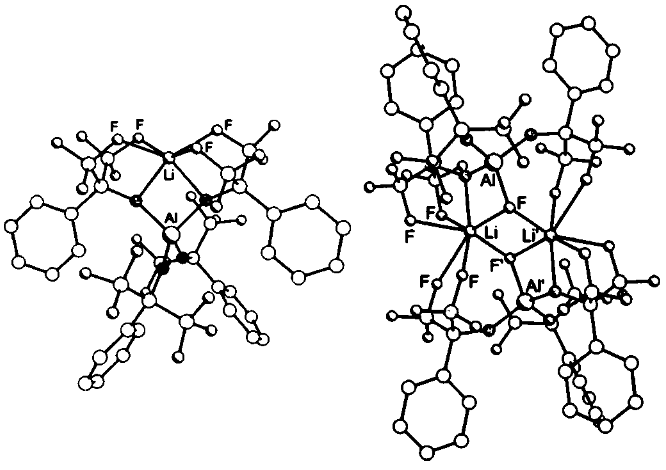


Figure 4. Drawings of the structures of the monomeric structure $LiAl(HFPP)_4$ (Ref. 12), left, and the centrosymmetric dimeric structure of $LiAlF(HFPP)_3$ (Ref. 22), right. The unlabeled shaded circles are fluorine atoms and the unlabeled plain circles are carbon atoms. Hydrogen atoms have been omitted for clarity. $HFPP^- = OCPh(CF_3)_2^-$.

The $LiAlF(HFPP)_3$ electrolyte is unique in that it contains a very polar Al-F bond with a strongly coordinating fluorine atom. The X-ray structures of $LiAl(HFPP)_4$[12] and $LiAlF(HFPP)_3$[22] are compared in Fig. 4. The latter structure contains a diamond-shaped Li_2F_2 core involving the fluorine atoms that are bonded to the Al atoms. One of the two Li-F(Al) bonds is 1.821(8) Å, shorter than any of the Li-O(Al) bonds in either structure, which range from 1.978(8) to 2.017(8) Å. Therefore, the presence of the Al-F bond in the $AlF(HFPP)_3^-$ anion renders this anion much more strongly coordinating (and, presumably, more strongly ion-pairing) than the $Al(HFPP)_4^-$ anion. This explains why the conductivity of $LiAlF(HFPP)_3$ in DME is so much lower than that of $LiAl(HFPP)_4$, despite the fact that the $AlF(HFPP)_3^-$ anion is smaller than $Al(HFPP)_4^-$. Consistent with this, σ_{max} for $LiAlF(HFPP)_3$, while lower than σ_{max} for $LiAl(HFPP)_4$, occurs at a higher concentration than for $LiAl(HFPP)_4$.

The 0.1, 0.2, and 0.3 M DME σ values for $LiPF_6$, which are also not shown, are lower than the corresponding values for four of the

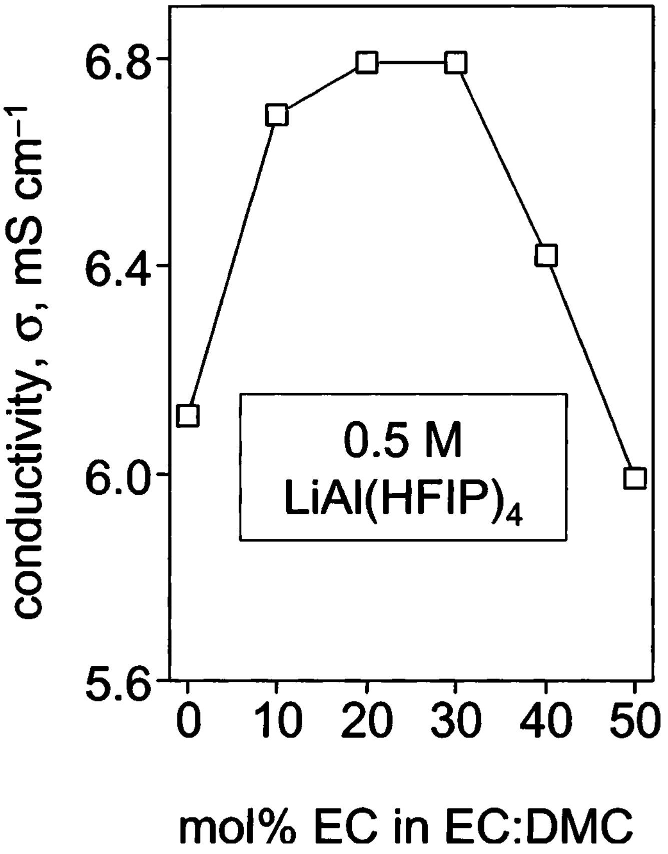


Figure 6. Conductivities of 0.5 M $LiAl(HFIP)_4$ solutions as a function of mol % EC in EC:DMC mixtures ($HFIP = OCH(CF_3)_2$).

six lithium aluminates (see Table I). We suggest that the PF_6^- anion, like the $AlF(HFPP)_3^-$ and $Al(TFE)_4^-$ anions, is more strongly associated with Li^+ in DME than are the four $Al(OCR(CF_3)_2)_4$ anions. In contrast, the EC:DMC σ values for $LiPF_6$ are higher than for $LiAl(HFIP)_4$ and $LiAl(HFPP)_4$, as shown in Fig. 5. This is probably due to both the higher viscosity and the higher dielectric constant of the EC:DMC mixture relative to DME. Nevertheless, the EC:DMC σ_{max} for $LiAl(HFIP)_4$, 6.3 mS cm^{-1}, is high enough for this thermally stable electrolyte to be considered as a replacement for $LiPF_6$ in secondary lithium-ion batteries.

We investigated whether 50:50 mol % EC:DMC was the optimum blend of these solvents for the $LiAl(HFIP)_4$ electrolyte. The results, shown in Fig. 6, show that a blend between 20:80 and 30:70 mol % EC:DMC is marginally better than the standard 50:50 mol % mixture.

Electrochemical stability.—The electrochemical stabilities of the $Al(HFIP)_4^-$ and $Al(HFPP)_4^-$ anions were investigated using cyclic voltammetry (CV). Negligible faradaic current was observed between 0 and 5.2 V *vs.* $Li^{+/0}$ (conditions: 0.1 M Li^+ salt in DME, glassy carbon working electrode, 5 mV s^{-1}). At potentials higher than 5.2 V, irreversible DME oxidation, and possible anion oxidation, occured. Below 0 V, plating of lithium was observed. The same results were obtained for a 0.1 M DME solution of $LiPF_6$. In addition, a 0.5 M EC:DMC solution of $LiAl(HFIP)_4$ did not undergo oxidation at potentials less than or equal to 5 V *vs.* $Li^{+/0}$. At potentials higher than 5 V, irreversible oxidation of EC, DMC, and/or the $Al(HFIP)_4^-$ anion occured.

Lack of reactivity with MCMB carbon, $LiCoO_2$, and aluminum.—CVs (not shown) of EC:DMC solutions of $LiAl(HFIP)_4$ (0.5 M) and $LiPF_6$ (1 M) using an MCMB carbon electrode were similar between 0 and 2 V *vs.* $Li^{+/0}$ (5 mV s^{-1} scan rate). In both cases, efficient reductive intercalation of Li^+ was observed. There were no other reactions of the electrolyte with the carbon electrode. The same was true for both electrolyte solutions when a $LiCoO_2$ electrode was used instead of the carbon electrode (the potential range investigated was 2.4-4.8 V *vs.* $Li^{+/0}$).

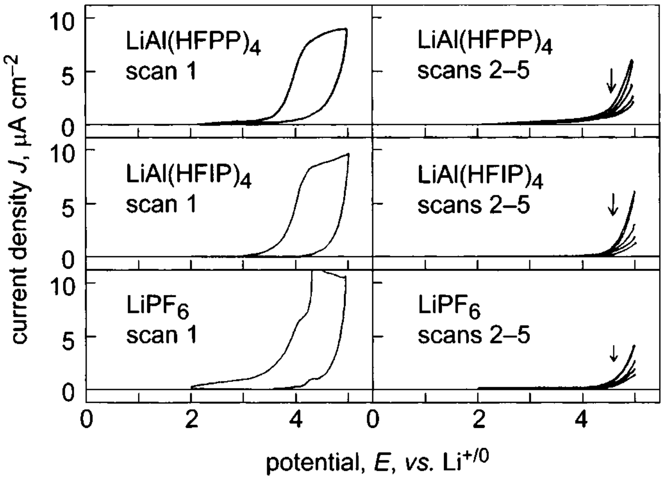


Figure 7. CVs of 0.3 M propylene carbonate solutions of $LiAl(HFIP)_4$, $LiAl(HFPP)_4$, and $LiPF_6$. Conditions: aluminum working electrode, lithium foil counter and reference electrodes, 10 mV s^{-1}).

The lack of any tendency of $LiAl(HFIP)_4$ and $LiAl(HFPP)_4$ to promote the corrosion of aluminum was investigated by cyclic voltammetry, chronoamperometry, and scanning electron microscopy (SEM). CVs for these two electrolytes and for $LiPF_6$ in PC using an aluminum working electrode are shown in Fig. 7. In each experiment, potentials between 2 and 5 V *vs.* $Li^{+/0}$ were scanned five times. Passivation of the electrode surface was evident for all three electrolytes during the first scan. By the fifth scan, the current density at 5 V was ≤ 2.2 μA cm^{-2}. After the fifth scan, each aluminum electrode was examined by SEM, and no evidence of corrosion (*i.e.*, pitting) was observed. In addition, new aluminum working electrodes were held at 5 V *vs.* $Li^{+/0}$ in each electrolyte solution for one hour. Again, no pitting of any of the three electrodes was observed by SEM.

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