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Lithium salts of bis(perfluoroalkyl)sulfonic acids: synthesis, characterization and conductivity studies

S.A. Ullrich [a], G.L. Gard [a,*], R.L. Nafshun [b], M.M. Lerner [b]

[a] *Chemistry Department, Portland State University, Portland, OR 97207-0751, USA*

[b] *Department of Chemistry and Center for Advanced Materials Research, Oregon State University, Corvallis, OR 97331-4003, USA*

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Abstract

Lithium salts of bis(perfluoroalkyl)sulfonic acids, $(CF_2)_n(SO_2OLi)_2 \cdot wH_2O$, where $n = 1$–4 (**1**–**4**), w = the number of waters of hydration, and $O(CF_2CF_2SO_2OLi)_2$ (**5**), were prepared by double decomposition and ion-exchange methods. Infrared, NMR and mass spectral data support the assigned structures. Thermal measurements indicate that these salts can be prepared free of acid and water impurities; the salts are stable up to 220 °C for the smallest anion, and above 400 °C for the largest anion. Impedance analyses were used to provide the bulk ionic conductivities of some poly(ethylene oxide)–salt complexes. Of these salts, **5** was found to have the highest conductivity: σ is about 5×10^{-6} Ω^{-1} cm^{-1} at 100 °C.

Keywords: Lithium salts; Bis(perfluoroalkyl)sulfonic acids; Synthesis; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

High interest in rechargeable solid-state lithium batteries [1] has lead to a search for lithium salts that will serve as lithium charge carriers in the polymer electrolyte portion of such batteries.

Bannister et al. have recommended that the dilithium salts of perfluoroalkyl disulfonic acids might be good candidates for high conductivity in polymer electrolyte work [2]. These salts contain large anions and bear a 2− charge; they can be expected to diffuse more slowly than the triflate ion, resulting in a decrease in the anionic current and thereby limiting the extent of irreversible polarization in poly(ethylene oxide) (PEO)–salt electrolytes. Also, Li ion transport numbers for highly-conducting polymer electrolytes are generally less than 0.5, so there is much room for improvement in this area. In general, however, the high lattice stabilization energies of simple salts of the type Li_2An or Li_3An will result in limited solubility or insolubility in polyethers. Another concern is the less oxidative stability of some highly charged anions. The bis-sulfonate salts, however, should be oxidatively robust and relatively soluble in polyethers due to a low charge/volume ratio. The following salts $LiO_3S\ (CF_2)_nSO_3Li \cdot wH_2O$, where $n = 1, 2, 3, 4$ and the ether salt $O(CF_2CF_2SO_3Li)_2$ were prepared and characterized. All compounds, except $CF_2(SO_3Li)_2 \cdot 3/2H_2O$, were then tested for conductivity in PEO at a ratio of eight oxygens from the PEO to one lithium from the salt; the ether salt was further tested at ratios of 16:1, 32:1 and 64:1.

2. Experimental details

2.1. Materials

The following chemicals were obtained from the 3M Company: $[CF_2(SO_2O)_2]Ba$, $[(CF_2CF_2SO_2O)_2]Ca$, $(CF_2SO_2OK)_2$, $CF_2(CF_2SO_2OK)_2$, $[(CF_2CF_2SO_2O)_2]Ca$ and $[O(CF_2CF_2SO_2O)_2]Ca$. These samples were used without further purification. The $LiOH \cdot H_2O$ was obtained from Matheson, Coleman and Bell. The $Li_2SO_4 \cdot H_2O$ and acetonitrile came from Mallinckrodt Chemical Company. The Amberlite IR-120 polystyrene sulfonate ion-exchange resin was a Rohm and Haas product. The poly(ethylene oxide) used to make the polymer–salt complexes came from Aldrich Chemical Company ($M_W = 5 \times 10^6$).

2.2. General procedures

A Nicolet 20-DX spectrometer was used to obtain infrared spectra. Solid samples were pelletized with KBr for analysis.

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* Corresponding author.

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Nuclear magnetic resonance spectra were obtained from two instruments. A Varian EM-390 spectrometer was used at 84.7 MHz for some of the ^{19}F NMR analyses. A Bruker AMX-400 instrument operating at 376.5 MHz for ^{19}F samples and at 100.6 MHz for ^{13}C samples was used for the rest of the NMR work. A D_2O lock was used instead of an internal standard because these compounds are appreciably soluble in water. Downfield is taken as the positive direction for the reporting of fluorine resonance values.

A Mel-Temp melting point apparatus served for the determination of the decomposition points for the salts; these decomposition points are reported without correction. A Vacuum Atmospheres Corporation Dri-Lab HE-43-2 was used for the manipulation of moisture-sensitive materials. Nitrogen gas, dried under a heated molecular sieve, was used as the dry box atmosphere. Moisture was kept below 10 ppm, the point at which titanium tetrachloride begins to fume in moist air [3].

The mass spectrometric work was accomplished using either a Varian MAT CH5 or a Finnigan MAT 8230 system operating at 70 eV. The fast atom bombardment (FAB) technique was employed in both positive and negative modes; samples were dissolved in glycerin prior to analysis. These analyses were performed at the Institute for Inorganic and Physical Chemistry at the University of Bremen, in Bremen, Germany. Multiple mass peaks for a given ion are due to isotopic combinations with lithium and sulfur. Elemental analyses were performed by Beller Microanalytical Laboratory in Göttingen, Germany. Differential scanning calorimetry was performed with 20–25 mg samples loaded in hermetically-sealed Al pans in the Shimadzu DSC-50Q. Salt samples were heated at 10 °C/min from 30 °C to 750 °C. Thermogravimetric analyses utilized the Shimadzu TGA-50. Salt samples (15–20 mg) were loaded into a Pt pan and heated from 30 °C to 750 °C at 10 °C min^{-1} under N_2 flow (50 ml min^{-1}).

2.2.1. *Synthesis of* $CF_2(SO_2OLi)_2 \cdot 3/2H_2O$ *(1)*

A 7.78 g (0.0224 mol) sample of $Ba[(OSO_2)_2CF_2]$ was digested with 2.85 g (0.0223 mol) of $Li_2SO_4 \cdot H_2O$ in 650 ml of water. The resulting mixture was allowed to digest for 4 d, then filtered through an ASTM 10–15 M fritted glass filter. The cloudy filtrate became clear on further filtration using Whatman No. 42 filter paper. The solution was then concentrated through evaporation on a rotary evaporator to a small volume, and dried in the frozen state under vacuum. Weight of product, 4.29 g; yield, 76.3%. This sample started to turn gray at 224 °C.

The infrared spectrum showed bands (cm^{-1}) at: 3522 (w); 3473 (w); 1631 (w); 1497 (w); 1434 (w); 1286 (st, shldr); 1265 (st); 1223 (st); 1117 (w); 1085 (w); 1072 (m); 1055 (w); 1039 (m); 955 (w); 938 (w); 711 (w, shldr); 698 (m); 620 (w, shldr); 610 (st); 568 (w); 545 (w). MS (*m/z*) (FAB)$^+$: 455 $(2M \cdot Li)^+$; 323 $(M \cdot C_3H_8O_3 \cdot Li)^+$; 231 $(M \cdot Li)^+$; 201 $(SO_2CF_2SO_2OLi^+$; 111 $CFSO_3^+$; 33 CH_2F^+; 31 CF^+: (FAB)$^-$: 665 $(3M-Li)^-$; 469 $(2M \cdot 3Li)^-$; 457–454 $(2M \cdot Li)^-$; 443/441/440 $(2M-Li)^-$; 423 $(M \cdot LiOSO_2CFSO_2OH)^-$; 311 $(M \cdot SO_3Li)^-$; 304 $(M \cdot SO_3)^-$; 233/231 $[CF_2(SO_3H)_2 \cdot F]^-$; 219/217/216 $SO_3CF_2SO_3Li^-$; 211 $HSO_3CF_2SO_3^-$; 199 $LiOSO_2CFSO_2OH^-$; 81 HSO_3^-. Analysis: Calc. for $CF_2(SO_3Li)_2 \cdot 3/2H_2O$: C, 4.78; H, 1.20; F, 15.1%. Found: C, 5.71; H, 1.39; F, 15.2%.

2.2.2. *Synthesis of* $(CF_2SO_2OLi)_2 \cdot 2H_2O$ *(2)*

An 11.31 g (0.0334 mol) sample of $(KOSO_2CF_2)_2$ was passed through two columns (140 ml total volume) of acid form Amberlite IR-120, having a resin capacity of 288 mequiv. H^+, to ensure quantitative conversion to the corresponding acid. The total residence time was 2 h; the rinse with three bed volumes of water (400 ml) took 1.5 h. The effluent and rinse solution mixture was neutralized with an $LiOH \cdot H_2O$ solution until the pH was 6.4. The total solution volume was then brought to under 20 ml, and dried under vacuum. Yield, 8.47 g or 86.5%. A previously prepared sample of the salt turned brown at 269 °C.

The infrared spectrum exhibited bands (cm^{-1}) at: 3571 (w, shldr); 3522 (w); 3409 (w, br); 1638 (w); 1427 (w); 1300 (st, shldr); 1272 (st, shldr); 1152 (st); 1137 (m, shldr); 1081 (m); 1056 (st); 845 (w); 654 (w, shldr); 626 (m); 561 (m); 526 (w). MS (*m/z*) (FAB)$^+$: 281 $(M \cdot Li)^+$; 155 $CF_2CF_2SOLi^+$; 111 $CFSO_3^+$; 101 $CF_2CF_2H^+$; 100 $CF_2CF_2^+$; 33 CH_2F^+; 32 CHF^+; 31 CF^+: (FAB)$^-$: 543/541/540 $(2M-Li)^-$; 369/368/367 $(2M-CF_2CF_2SO_3H)^-$; 361 $(M \cdot SO_3Li)^-$; 269–266 $(M-Li)^-$; 261 $(M \cdot H-2Li)^-$; 183/181 $CF_2CF_2SO_3H^-$; 177 $SCF_2CFSO_2^-$; 163/161 $CF_2CFSO_3^-$; 81 HSO_3^-; 80 SO_3^-; $C_2F_2 \cdot H_2O^-$; 19 F^-. Analysis: Calc. for $(CF_2SO_3Li)_2 \cdot 2H_2O$: C, 7.75; H, 1.30; F, 24.5%. Found: C, 8.36; H, 1.39; F. 24.2%.

2.2.3. *Synthesis of* $CF_2(CF_2SO_2OLi)_2 \cdot 2H_2O$ *(3)*

A 4.10 g (0.0106 mol) portion of $CF_2(CF_2SO_2OK)_2$ was dissolved in 60 ml of water and passed through 70 ml of acid form Amberlite IR-120 ion-exchange resin having a capacity of 144 mequiv. H^+. The column was rinsed with 200 ml of deionized water; residence and rinsing times together amounted to 1.5 h. A 0.92 g portion of $LiOH \cdot H_2O$ and small additions of lithium hydroxide solution were used to bring the pH of the combined solution of effluent and rinsings to 8.1. The solution was reduced in volume to less than 25 ml and freeze-dried under vacuum. The white powder weighed 3.41 g representing an 89.7% yield. This powder turns gray at 295 °C.

Infrared bands (cm^{-1}) were found at: 3592 (w); 3508 (w); 1638 (m); 1317 (st, shldr); 1305 (st, shldr); 1248 (st, br); 1175 (m); 1161 (m); 1148 (m); 1100 (m); 1063 (st); 1046 (m, shldr); 1012 (m); 987 (w); 847 (w); 780 (w); 712 (w); 666 (st, br); 607 (w); 584 (w); 569 (w); 546 (w); 532 (w); 482 (w); 461 (w). MS (*m/z*) (FAB)$^+$: 155 $CF_2CF_2SOLi^+$; 111 $CFSO_3^+$; 101 $CF_2CF_2H^+$; 33 CH_2F^+; 32 CHF^+; 31 CF^+: (FAB)$^-$: 643–640 $(2M-Li)^-$;

555 $(M\cdot CF_2CF_2CF_2SO_3H)^-$; 343 $(M\cdot F)^-$; 319–316 $(M-Li)^-$; 279 $OSCF_2CF_2CF_2SO_3H^-$; 233/231 $CF_2CF_2CF_2SO_3H^-$; 232/230 $CF_2CF_2CF_2SO_3^-$; 211 $CF_2CFCF_2SO_3^-$; 130 $CF_2SO_3^-$; 80 SO_3^-, $C_2F_2\cdot H_2O^-$. Analysis: Calc. for $CF_2(CF_2SO_3Li)_2\cdot 2H_2O$: C, 10.01; H, 1.12; F, 31.7%. Found: C, 9.74; H, 0.99; F, 30.1%.

2.2.4. Synthesis of $(CF_2CF_2SO_2OLi)_2\cdot 3/2H_2O$ (4)

A 5.53 g portion of Ca $[(OSO_2CF_2CF_2)_2]$ (0.0139 mol) was converted into the acid form by dissolving it in 60 ml of water and passing it through 70 ml of acid form Amberlite IR-120 ion-exchange resin having 144 mequiv. H^+ resin capacity. The resin was then washed with approximately 200 ml of water; residence and washing times together amounted to 1.5 h. The combined effluent and rinse solutions were then neutralized with $LiOH\cdot H_2O$ to give a resulting solution of pH 7.0. This solution was then reduced in volume to less than 25 ml by evaporation and freeze-dried under vacuum. A 4.83 g sample of white powder resulted, representing a yield of 95.8%. A portion of the powder turned dark when heated to 312 °C.

The infrared spectrum exhibited the following bands (cm^{-1}): 3634 (w, shldr); 3501 (m); 3459 (m, br); 1666 (w, shldr); 1631 (m); 1518 (w); 1427 (w); 1270 (st); 1253 (st, shldr); 1187 (m); 1164 (m); 1124 (st); 1044 (st); 865 (w); 736 (w); 730 (w); 679 (m); 619 (m); 588 (w); 559 (w); 539 (w); 493 (w); 471 (w). MS (*m/z*) $(FAB)^+$: 155 $CF_2CF_2SOLi^+$; 111 $CFSO_3^+$; 100 $CF_2CF_2^+$; 33 CH_2F^+; 32 CHF^+; 31 CF^+; $(FAB)^-$: 741 $(2M-Li)^-$; 393 $(M\cdot F)^-$; 369–366 $(M-Li)^-$; 281 $(CF_2)_4SO_3H^-$; 280 $(CF_2)_4SO_3^-$; 263/261 $C_4F_7SO_3^-$; 161 $CF_2CFSO_3^-$; 131 $C_3F_5^-$; 80 SO_3^-, $C_2F_2\cdot H_2O^-$; 19 F^-. Analysis: Calc. for $(CF_2CF_2SO_3Li)_2\cdot 3/2H_2O$: C, 11.98; H, 0.75; F, 37.9%. Found: C, 12.37; H, 0.84; F, 37.7%.

2.2.5. Synthesis of $O(CF_2CF_2SO_2OLi)_2$ (5)

A 5.00 g portion (0.0120 mol) of $Ca[(OSO_2CF_2CF_2)_2O]$ was dissolved in 20 ml of water and passed through 70 ml of acid form Amberlite IR-120 ion-exchange resin having 144 mequiv. H^+ capacity over a period of 1.5 h. The column was then washed with 200 ml of water. A solution prepared from the effluent and washings was neutralized with $LiOH\cdot H_2O$ until the solution pH was 7.0. The solution of the ether salt was slowly concentrated by evaporation at 40 °C; the concentrate was then frozen and allowed to dry under vacuum. A white powder, 2.64 g, was obtained corresponding to a yield of 60.8%.

The infrared spectrum of the product showed the following bands (cm^{-1}): 3508 (m); 3445 (m, br, shldr); 2924 (w); 2854 (w); 1642 (m); 1346 (m, shldr); 1280 (st, shldr); 1244 (st); 1165 (st); 1085 (m); 1068 (m); 1020 (m); 973 (m); 850 (w); 749 (w); 670 (w, shldr); 655 (m); 629 (w, shldr); 554 (w), 535 (w); 514 (w); 500 (w); 489 (w); 477 (w); 462 (w). MS (*m/z*) $(FAB)^+$: 155 $CF_2CF_2SOLi^+$; 111 $CFSO_3^+$; 101 $CF_2CF_2H^+$; 100 $CF_2CF_2^+$; 33 CH_2F^+; 31 CF^+: $(FAB)^-$: 773 $(2M-Li)^-$; 385–382 $(M-Li)^-$; 297 $HOSO_2(CF_2)_2O(CF_2)_2^-$; 296 $OSO_2(CF_2)_2O(CF_2)_2^-$; 277 $CFCF_2O(CF_2)_2SO_3^-$; 177 $OCF_2CFSO_3^-$; 161 $CF_2CFSO_3^-$; 117 $HOCF_2CF_2^-$; 80 SO_3^-, $C_2F_2\cdot H_2O^-$.

2.3. Electrochemical analysis of polymer complex

2.3.1. Preparation of $PEO_x(LiSO_3CF_2CF_2)_2O$

The salt was thoroughly dried under vacuum at 120 °C for 48 h to remove residual water or solvents. The poly(ethylene oxide) (PEO)–salt complexes were prepared by co-dissolution of salt and PEO at the required stoichiometry in acetonitrile. Complexes were dried in vacuo for 48 h and maintained under an inert atmosphere. Stoichiometries are described by $PEO_x(LiSO_3CF_2CF_2)_2O$, where x reflects the mole ratio of ethoxy repeats to Li ion.

2.3.2. Characterization of $PEO_x(LiSO_3CF_2CF_2)_2O$

Bulk ionic conductivities were measured on 1/2 in pressed pellets of the complexes in a hermetically-sealed cell using the Solartron 1260 impedance analyzer. Samples were heated to 100 °C and then quenched below −30 °C prior to data collection. Responses were measured from 12 MHz to 0.1 MHz between −30 °C and 100 °C. Bulk conductivities were derived from the high-frequency touchdown of Nyquist plots and known cell geometries.

2.3.3. Electrochemical work with other salts

Similar products were used for the preparation and characterization of PEO complexes with salts **2**, **3** and **4**.

3. Results and discussion

Two methods were employed for the synthesis of the dilithium salts of the bis(perfluoroalkyl)sulfonic acids. One method involved the reaction of lithium sulfate with the barium salt of the sulfonic acid:

$$Li_2SO_4\cdot H_2O + Ba(OSO_2)_2CF_2 \longrightarrow BaSO_4 + \underset{\mathbf{(1)}}{(LiOSO_2)_2CF_2} + H_2O$$

The other method involved the preparation of a sulfonic acid from its corresponding potassium or calcium salt by passing an aqueous solution of the corresponding salt through polystyrene sulfonic acid ion-exchange resin. The acid was then neutralized using lithium hydroxide.

$$KOSO_2(CF_2)_nSO_2OK \xrightarrow{\text{ion exchange}} HOSO_2(CF_2)_nSO_2OH$$

$$2LiOH + HOSO_2(CF_2)_nSO_2OH \longrightarrow \underset{\mathbf{(2,\,3)}}{LiOSO_2(CF_2)_nSO_2OLi + 2H_2O}$$

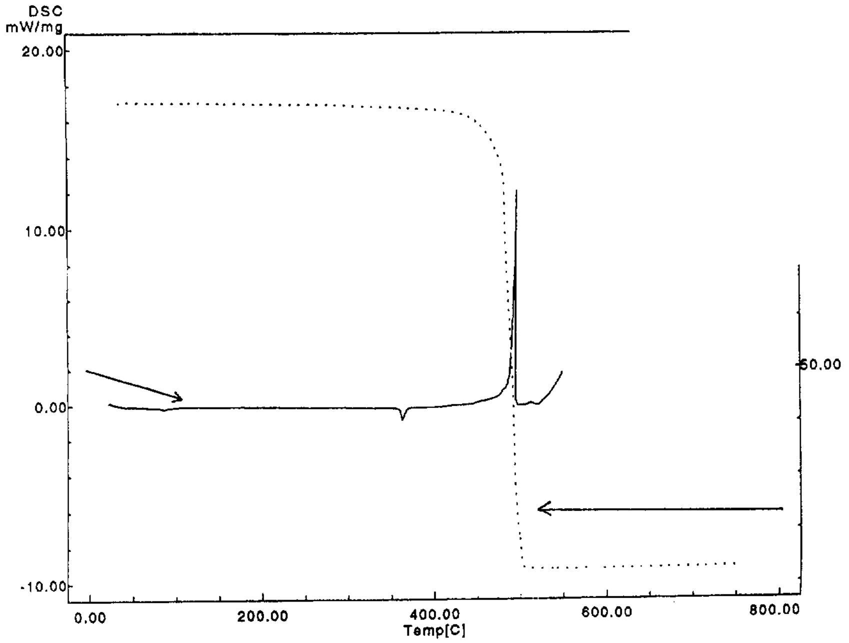

Fig. 1. TGA and DSC traces for $O(CF_2CF_2SO_2OLi)_2$.

$$Ca(OSO_2CF_2CF_2)_2 \xrightarrow{\text{ion exchange}} (HOSO_2CF_2CF_2)_2$$

$$2LiOH + (HOSO_2CF_2CF_2)_2 \longrightarrow (LiOSO_2CF_2CF_2)_2 + 2H_2O$$

(4)

$$Ca(OSO_2CF_2CF_2)_2O \xrightarrow{\text{ion exchange}} (HOSO_2CF_2CF_2)_2O$$

$$2LiOH + (HOSO_2CF_2CF_2)_2O \longrightarrow (LiOSO_2CF_2CF_2)_2O + 2H_2O$$

(5)

None of these compounds had sharp melting points; they all decomposed. An increase in the decomposition point of compounds **1**–**5** was seen: 224 °C for **1**; 264 °C for **2**; 295 °C for **3**; 312 °C for **4**; and about 450 °C for **5**. The DSC/TGA data provided in Fig. 1 indicate a single, sharp exothermic decomposition point for $O(CF_2CF_2SO_2OLi)_2$ at ca. 450 °C, indicating that the sample was free from volatile impurities such as water or the free acid. The purity of the salt is significant in considering the conductivity data obtained.

The interpretation of the infrared spectra of these perfluorinated sulfonic acid lithium salts is complicated by the fact that the C–F stretch of the CF_2 group (1100–1300 cm^{-1}) [4–6] appears in the same region of the spectrum as the SO_3 symmetric (1050–1100 cm^{-1}) and asymmetric (1180–1280 cm^{-1}) stretches [4,7,8]. Literature values for these types of compounds would lead us to assign the symmetric SO_3 stretch for our salts to the 1044–1072 cm^{-1} region, the asymmetric stretch to the 1244–1265 cm^{-1} region and the C–F stretch of CF_2 to the 1117–1300 cm^{-1} region. The C–O–C stretch is usually found at 1060–1150 cm^{-1} [5]; the 1165 cm^{-1} vibration for **5** was designated as a C–O–C stretch.

The fast atom bombardment (FAB) technique was applied for the analysis of our samples; it had been used to advantage before in the characterization of perfluoroalkyl sulfonates [9]. Runs producing both positive and negative ions were made. Cluster ions, some of high molecular weight, are a feature found in FAB mass spectra of perfluoroalkyl sulfonates [10]. For our samples, some of these had high relative intensity; for **1**, negative mode gave: $(2M-Li)^-$ (21.64); $(2M\cdot Li)^-$ (18.66); $(2M\cdot 3Li)^-$ (10.62); $(3M-Li)^-$ (1.98); $(3M\cdot Li)^-$ (1.38). No molecular ions were found in either the positive or negative mode runs.

The ^{19}F NMR spectra of compounds **1**–**4** (Table 1) showed CF_2 resonances that are in line with the literature values for the corresponding acids and potassium or sodium salts [11–13]. The chemical shift value for fluorines $O_3SCF_2SO_3$ is $\varphi = -107$ ppm; the range for fluorines $CF_2CF_2SO_3$ is $\varphi = -[114.3–115.3]$ ppm; and the range for fluorines

Table 1
^{19}F NMR spectra of dilithium perfluoroalkyl sulfonate salts

Compound	Inner carbons [a] φ (ppm)	Outer carbons [b] φ (ppm)
1		−107 (s)
2		−114.6 (s)
3	−120.3 (m)	−114.3 (m)
4	−122 (m)	−115.3 (m)
	CF_2S carbons φ (ppm)	CF_2O carbons φ (ppm)
5	−83.3 (s)	−120.0 (s)

[a] Band center of multiplets; inner carbons attached to carbon only.
[b] Band center of multiplets; outer carbons attached to sulfur.

Table 2
^{13}C NMR spectra of dilithium perfluoroalkyl sulfonate salts

Compound	Inner carbons [a] δ (ppm)	Outer carbons [b] δ (ppm)	$^1J_{CF}$ (Hz)	$^2J_{CF}$ (Hz)
1		119.0 (t)	310	
2		115.5 (t, t)	288	37.0
3		115.6 (t, t)	292	36.5
	112.7 (t, p)		264	32.3
4		115.2 (m)	291	34
	112.7 (t, p)		269	32
	CF_2S carbons δ (ppm)	CF_2O carbons δ (ppm)	$^1J_{CF}$ (Hz)	$^2J_{CF}$ (Hz)
5	111.6 (m)		290	31.8
		116.4 (m)	290	37.2

[a] Band center of multiplets; inner carbons attached to carbon only.
[b] Band center of multiplets; outer carbons attached to sulfur.

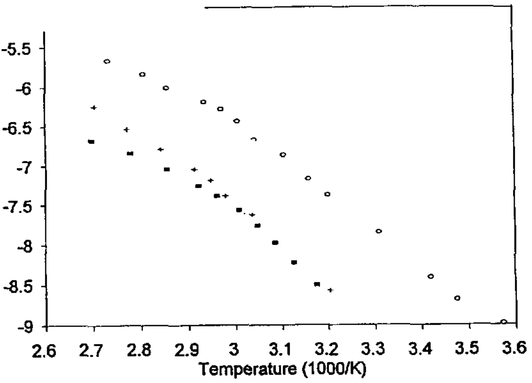

Fig. 2. Arrhenius plots for $CH_2CH_2O/Li = 8{:}1$ complexes of salts 2(−), 3(+) and 4(0).

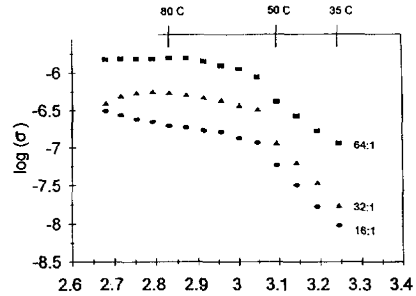

Fig. 3. Arrhenius plots for PEO complexes with $O(CF_2CF_2SO_2OLi)_2$ at CH_2CH_2O/Li mole ratios of 64:1, 32:1 and 8:1.

$CF_2CF_2CF_2$ is $\varphi = -[120\text{–}122]$ ppm. The resonance values for the fluorines in these lithium salts agree with the literature values for the corresponding acids and the corresponding potassium salts.

The fluorine resonances for **1** and **2** were singlets; the resonances for **3** and **4** were unresolved multiplets, as was found to be the case for $CF_2(CF_2SO_2F)_2$ [14].

In Table 2, the ^{13}C spectral data for compounds **1**–**5** are presented. The chemical shifts agree with the values reported for the two-, three- and four-carbon acids and salts [12]. For **1**–**4**, the chemical shift value for carbons CCF_2C is $\delta = 112.7$ ppm and the range for carbons CF_2S is $\delta = 115.2\text{–}119$ ppm. The coupling constant range for these compounds is 264–310 Hz for $^1J_{CF}$ and 32–37 Hz for $^2J_{CF}$. A spectrum of **5** showed multiplets for both CCF_2S and CCF_2O carbons.

Two Arrhenius plots, Figs. 2 and 3, are provided to summarize the impedance data. Fig. 2 contains Arrhenius plots of the data obtained at the stoichiometry $OCH_2CH_2/Li = 8{:}1$ for PEO complexes with salts **2**–**4**. The response is nearly linear over the temperature range evaluated: the similar slopes of these lines indicate that the activation energies for ionic conduction are all approximately 0.15 eV for these complexes. The curvature evident upon close inspection of the data is associated with Vogel, Tammann, Fulcher (VTF) behavior that arises from ion conduction through a polymeric matrix [15]. Above 75 °C, the conductivities for all these complexes are 2–3 orders of magnitude lower than those of PEO complexes with $LiCF_3SO_3$ or $LiClO_4$ at similar stoichiometries [16]. Some part of this decrease might be ascribed to the lower diffusion rate of the larger anions, but that will not cause a change of this magnitude. The effect may arise either from changes in the extent of polymer complex crystallinity or slower polymer dynamics due to association with the more highly charged anions. The conductivity is significantly higher for complexes of **4** than for complexes with the others. Two possible explanations are the increased separation of anionic groups and the corresponding decrease in the anionic charge density, or a change in the solubility of the salt.

Fig. 3 shows the effect of stoichiometry on the ionic conductivities of the PEO complexes formed with $O(CF_2CF_2SO_2OLi)_2$. The conductivities decrease with salt content, and are again significantly lower than those obtained with simple salts such as $LiCF_3SO_3$.

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