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Syntheses of a wide family of new aryl based perfluorosulfonimide lithium salts. Electrochemical performances of the related polymer electrolytes

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1. Introduction

Moving from lithium-ion batteries dedicated to the 4C mass market (computers, cellular phones, camcorders, cordless tools) to lithium batteries addressing the electric vehicle market requires (i) improving the safety level (toxicity, flammability etc.) and (ii) a clever battery recycling allowing most of the components to be reused. In current lithium-ion batteries the salt providing the best performances is the lithium hexafluorophosphate, LiPF₆. The latter belongs to the family of $LiXF_n$ and involves a coordinate bond or dipolar bond. Following the formation of this bond, the whole of the X-F bonds is indiscernible but the coordinate bond induces a chemical weakness of the anion. This family of anions that include BF₄⁻, AsF₆⁻, PF₆⁻, SbF₆⁻, are therefore subjected to disproportionate into the Lewis acid XF_{n-1} [1]. Among the related lithium salts, the more appropriate one is LiPF₆. Indeed LiBF₄ leads to lower electrolyte conductivities, LiAsF₆ is suspected to be carcinogenic and LiSbF₆ has a limited stability in reduction. Additionally, it has been recently reported that LiPF₆, whose thermal stability (\sim 50 °C and around 80 °C in solution) is very limited [2], can lead to

ABSTRACT

This paper reports both on a general multistep synthesis of a wide family of aryl substituted perfluorosulfonimides and on a preliminary electrochemical investigation of two lithium salts hosted by a poly(oxyethylene) homopolymer. Both salts have a cationic transference number more than twice that of LiTFSI. Additionally, one of these salts exhibits markedly higher cationic conductivities than POE/LiTFSI electrolytes. These preliminary data are very encouraging as, thanks to the aryl moiety, a wide variety of salts can be considered in order to still improve the performances of polymer electrolytes.

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dangerous degradation by-products [3]. This thermal stability is crucial as it will be very difficult and probably costly to avoid the heating of a battery pack. Last, its recycling would not allow LiPF_6 to be easily reused. Among, the alternatives to the previous salts, LiBOB, lithium bis(dioxalato) borate [4] is probably the most famous. Its synthesis is non-costly and it provides a good SEI on lithium graphite electrode but its dissolution in aprotic carbonate solvents is limited, leading to fairly low salt concentrations in current electrolytes. A review reports on various fluorinated forms of LiBOB and on lithium tetrakis(polyfluoroalkoxy) aluminate [5]. In order to overcome the LiPF₆ issues, fluoro(perfluoroalkyl) lithium phosphates were also proposed [6].

Lithium triflate LiCF₃SO₃, lithium methide used name of tris(trifluoromethylsulfonyl)methane LiC(CF₃SO₂)₃ and lithium bis(trifluoromethylsulfonyl) amide abbreviated as LiTFSI LiN(CF₃SO₂)₂ are thermally, chemically and electrochemically stable lithium salts. As in the previous salts i.e. LiXF_n, the related anions are the conjugated bases of superacids. Unfortunately, the first one leads to poor conductivities in liquid and polymer electrolytes while the second one, whose molar mass exceeds 400 g, provides high conductivities in polymer electrolyte [7]. As for LiTFSI, it exhibits high conductivities in poly(oxyethylene) based electrolytes [8]. TFSI⁻, a fairly hard anion [9], benefits from a large delocalization of its negative charge as evidenced

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by *ab initio* calculations while the conformational analysis showed that the total energy calculated for the rotation around the nitrogen atom is very low [9,10]. The large delocalization of the negative charge is an asset for the ion-pair dissociation in aprotic medium that, in addition to the high flexibility of the anion, leads to high conductivities. Another asset lies in its high oxidative stability that is in agreement with the fairly high hardness of TFSI anion. D. DesMarteau who invented the TFSI anion did a fruitful review of perfluorosulfonimide anions [11]. The cationic transference numbers, T^+ , are however lower than most of the lithium salts [12–14]. It can be emphasized that, despite its anion bulkiness, lithium methide leads also to very low cationic transference numbers in poly(oxyethylene), POE, based host polymers [14].

Whatever its advantages TFSI anion cannot be modified in such a way to incorporate extra functionalities as, for instance, polar [15] or plasticizing moieties. In order to take advantage of the outstanding properties of perfluorosulfonimides while modulating their physicochemical properties a multistep synthesis strategy has been conceived. In this contribution we will describe this strategy and provide the preliminary data obtained with two perfluorosulfonimide salts.

2. Results and discussion

In order to synthesize dissymmetric perfluorosulfonimide salts bearing an aryl moiety a multistep strategy starting from thiophenol has been selected. Thereafter the performances of polymer electrolytes based on two lithium salts were investigated.

2.1. Synthesis of new sulfonamide lithium salts

Recently, we described a new and general synthesis of (trifluoromethyl)-(perfluoroalkyl)sulfonimide lithium and triethylammonium salts **1** in which the perfluoroalkyl chain is substituted, at the ω position, by an aryl sulfanyl, an arylsulfinyl or an arylsulfonyl moiety (Scheme 1) [16a,b].

These salts were prepared from original ω -(arylsulfanyl)perfluoroalkylsulfonyl fluorides (or their sulfinyl or sulfonyl congeners) **2**, arising from ω -(arylsulfanyl)-perfluoroalkyl bromides, as we previously described (Scheme 2) [17a,b].

The key intermediate from **2** to **1** (which does not need to be isolated) is the corresponding N-benzyl-sulfonimide **3** which, surprisingly, was easily debenzylated, under very mild conditions and without any hydrogen or metallic catalyst, by a simple treatment, at room temperature, with a nucleophile such as ethanol, followed by neutralization of the resulting (trifluor-omethyl)(perfluoroalkyl)sulfonimide oxonium salt (Scheme 3) [16]. Such an easy debenzylation, occurring through a simple



Scheme 1. General structure of described sulfonimide salts.

nucleophilic substitution around the benzylic carbon, is due to the huge leaving ability of the perfluoroalkylsulfonimide moiety.

This method has been also extended to the synthesis of $[(CF_3CF_2O-(CF_2)_2SO_2)(CF_3SO_2)N]^-\ M^+\ (M=Li^+,\ Et_3NH^+).$

In a previous paper, we described complementary methods for the deprotection of symmetrical N-benzyl or N-allyl (perfluoroalkyl)sulfonimides which allow preparing salts in which the (perfluoroalkyl)sulfonimide anion is associated with a very large panel of metallic or onium cations [18]. These methods have been largely exemplified from N-benzyl or N-allyl triflimide but were also applied to the preparation of symmetrical perfluoroalkylsulfonimides as TFSI [(CF_3SO_2)₂N]⁻ M⁺ (Scheme 4). Moreover, there is no doubt that they can be used to debenzylate **3** under various conditions.

In order to obtain the broadest range cations and to use their most available and convenient sources, three types of nucleophiles have been used for the deprotection of N-benzyl (or allyl) (perfluoroalkyl)sulfonimides: (1) as above, ethanol associated with various bases such as metallic and ammonium hydroxides (LiOH, KOH, Ca(OH)₂, Zn(OH)₂, Me₄N⁺OH⁻), metallic oxides (Sc₂O₃, Ag₂O), metallic carbonates and hydrogenocarbonates (NaHCO₃, MgCO₃), organometallics (ZnEt₂, LiN(TMS)₂) or amines (Et₃N, ⁱPr₂EtN); (2) onium halides (ⁿBu₄N⁺ Br⁻, Me₃S⁺ I⁻, MePh₃P⁺ Br⁻); (3) amines, imidazoles or phosphines (Et₃N, ⁱPr₂NH, N–Me imidazole, Ph₃P) which led to benzylonium cations Bn–R₃⁺ (R = N, P).

It must be noticed that the two last methods are the most appropriated to reach anhydrous (perfluoroalkyl)sulfonimide salts.

2.2. Polymer electrolytes based on aryl lithium arylsulfonimide salts

Two salts, **Salts 1** and **2**, whose structures are provided in Scheme 5, were investigated.

Due to its high crystallinity and to its poor mechanical performances above the melting point, poly(oxyethylene) host polymer POE is not the best polymeric matrix, but it remains the reference host polymer for polymer electrolytes free of molecular solvent. Therefore the preliminary assessments of these new salts were performed on the POE complexes.

$$\begin{array}{c} \text{PhSH} \xrightarrow[]{m = 1 (3 \text{ eq})}{m = 2 (1.25 \text{ eq})} \\ \text{PhSH} \xrightarrow[]{m = 2 (1.25 \text{ eq})}{NaH (1.5 \text{ eq})} \\ \xrightarrow[]{\text{DMF}}{-40^{\circ}\text{C to r.t.}} \\ \begin{array}{c} \text{PhS-(CF_2)_mBr} \\ \text{isolated} \\ -40^{\circ}\text{C to r.t.} \\ m = 1; 62 \% \\ m = 2; 90 \% \\ \end{array} \\ \begin{array}{c} \text{Mg (2 eq)} \\ \overrightarrow{\text{THF}} \\ -78^{\circ}\text{C to r.t.} \\ m = 1; 92 \% \\ m = 2; 90 \% \\ \end{array} \\ \begin{array}{c} \text{F-TEDA (1 eq)} \\ \overrightarrow{\text{CH}_3\text{CN}} \\ -40^{\circ}\text{C to r.t.} \\ \end{array} \\ \begin{array}{c} \text{PhS-(CF_2)_mSO_2^{\ominus}} \\ m = 2; 90 \% \\ \end{array} \\ \begin{array}{c} \text{F-TEDA (1 eq)} \\ \overrightarrow{\text{CH}_3\text{CN}} \\ -40^{\circ}\text{C to r.t.} \\ \end{array} \\ \begin{array}{c} \text{PhS-(CF_2)_mSO_2\text{F}} \\ \text{isolated} \\ m = 1; 57 \% \\ \overrightarrow{\text{2}} \\ m = 2; 68 \% \\ \end{array} \end{array}$$

Scheme 2. Synthesis of ω-(arylsulfanyl)perfluoroalkylsulfonyl fluorides.



Scheme 4. Access to various (perfluoroalkyl)sulfonimides salts.

2.2.1. Thermal analyses of POE electrolytes

2.2.1.1. DSC analyses of POE electrolytes. Both new salts induce a decrease in the melting points of the polymer electrolytes, as compared to POE. This decrease depends on the salt concentration and seems to be similar for both electrolytes (Table 1).

It is well-known that the salt interaction with the POE matrix induces an increase in the glass transition temperature T_g . This effect is often called transient cross-linking. This T_g increase which is clearly evidenced in amorphous electrolytes is however partially screened in semi-crystalline electrolytes as the crystalline phase constrains the amorphous one. The comparison of POE electrolyte's T_g based on both salts is provided in Table 1.

2.2.1.2. TGA analyses. As the thermal stability of POE in air is questionable above 130 °C, the thermogravimetric analyses (TGA) were restricted to both salts. The TGA traces show that the onset of weight loss starts from 160 and 225 °C respectively for **Salts 1** and **2**. The presence of an additional CF₂ induces a neat thermal stability increase in air. The latter can be related to an increase in the electron withdrawing effect induced, in **Salt 2**, by the additional CF₂ that decreases the electronic density on the sulfur atom of the thioether. Both salts are however sufficiently stable (i) to meet the thermostability requirements of a lithium-polymer battery and (ii) to allow an easy recovery to be performed following a battery recycling.



Scheme 5. Formula of Salts 1 and 2.

Table 1Thermal characteristics of Salts 1 and 2.

O/Li (mol/mol)	Salt 1			Salt 2			
	$T_{\rm g}(^{\circ}{\rm C})$	$T_{\rm f}(^{\circ}{\rm C})$	ΔH (J/g)	T_{g} (°C)	$T_{\rm f}(^{\circ}{ m C})$	$\Delta H (J/g)$	
12	-30	33	30	-31	36	40	
20	-30	47	65	-31	48	72	
30	-32	51	80	-	-	-	



Fig. 1. Conductivity dependence on temperature.

2.2.2. Conductivity measurements

The conductivities were measured in the temperature range 20-80 °C. The Arrhenius plots of POE electrolytes based on both salts i.e. Salts 1 and 2 are gathered in Fig. 1. As usual in POE electrolytes the conductivity dependence on temperature follows an Arrhenius law and a VTF one respectively below and above the melting point $T_{\rm m}$. The conductivity decrease around the melting temperature is more pronounced at the lowest salt concentrations i.e. 30 and 35, in relation with a plasticizing effect of the salts. The conductivities, at 80 °C, of the two types of electrolytes exceed 0.2 mS/cm making them candidates for the application. The conductivity maxima, measured at 80 °C and at a concentration O/Li = 20 for POE/Salt 1, reaches a very encouraging value i.e. 0.6 mS/cm. This one is however lower than that obtained using LiTFSI/POE electrolytes. While in the analogues based on lithium sulfonates i.e. C₆H₅-S-CF₂-SO₃Li and C₆H₅-S-CF₂-CF₂-SO₃Li [19] the POE electrolytes based on the former were found slightly less conductive than the latter, in the case of sulfonimides, POE/Salt 1 that bears only one CF₂, is roughly twice more conductive than POE/Salt 2. This result was unexpected as the tetrafluoroethylene moiety should (i) increase the electron withdrawing effect and therefore the ion pair dissociation and (ii) increase the anion flexibility. It seems therefore that the molecular weight of the anion has a higher impact on the electrolyte conductivity than the dissociation, which is already probably sufficient in Salt 1.

2.2.3. Cationic transference numbers

Although obtaining high conductivities is essential to minimize the polymer electrolyte contribution to the internal resistance of the battery, the knowledge of its cationic transference number, T^+ , is required to assess their performances in batteries. Indeed, on the one hand the cationic transference number has an impact on the formation of concentration gradients in the electrolyte during the battery operation and, on the other hand, it allows the cationic conductivity σ^+ to be calculated, which is the relevant parameter for an electrolyte. Cationic transference numbers, T^+ , and cationic conductivities, σ^+ , are presented in Table 2.

The cationic transference numbers of the polymer electrolytes (measured at 70 °C) roughly range between 0.2 and 0.26. They depend both on the type of POE/salt electrolytes and on the salt concentration. The measured T^+ are close to those previously measured, in poly(oxyethylene) host polymers, with usual lithium salts as lithium perchlorate or lithium iodide [14] but lower than

those determined, in the same conditions, for the lithium sulfonate analogues of Salts 1 and 2 [19]. On the other hand they are markedly higher than those of POE/LiTFSI that laboriously reach 0.1 [12,14]. The high cationic conductivity maxima determined for POE/**Salt 1** must be emphasized as it is roughly the double of the value obtained with POE/LiTFSI.

2.2.4. Cyclic voltammetry

The cyclic voltammetry was performed using 2 support electrolytes. The first one, acetonitrile + NBu₄PF₆, is well-adapted to check the oxidative stability of the salts but unsuitable to explore the stability of the salts at low potentials. The second one was a solution of N(Et)₄ClO₄ in propylene carbonate. The cathodic and anodic peaks are presented in Table 3.

Salts 1 and **2** exhibit a wide electrochemical stability window and, in particular, a good stability towards the reduction. They also show a better stability towards the oxidation than their sulfonate analogues, whose anodic peaks are respectively 5.1 and 5.3 V vs Li/ Li⁺ [19]. The sulfonimide moiety shifts therefore the stability towards the oxidation by at least 200 mV. On the other hand, the **Salt 2** is more stable towards the oxidation than the **Salt 1**. It may be inferred that the additional CF₂ in **Salt 2** decreases the electronic density on the sulfur atom, thus increasing its stability towards the oxidation.

Та	ble	2

Table 3

Cationic transference numbers and cationic conductivities of polymer electrolytes.

$^{++}(S cm^{-1})$
0 ⁻⁵ 0 ⁻⁴
) ⁻⁵ 0 ⁻⁵ 0 ⁻⁵

Electrochemical	stability	windows	of	Salts	1	and	2.

Lithium sulfonimide salts	Cathodic peak (V vs Li/Li ⁺)	Anodic peak (V vs Li/Li ⁺)
Salt 1	<0.3	5.4
Salt 2	<0.3	5.6

3. Conclusion

These new multistep organic syntheses provide routes to a variety new fluorinated organic anions. The starting thiophenol synthon allows, through a clever selection of suitable substituted thiophenols, a variety of salts based on multifunctional anions to be designed as, for instance, ionic liquids, which could be useful in several electrochemical energy storage and conversion applications. At this stage, due to the organic constraints, only a few amounts of materials were prepared, restricting therefore the scope of our investigations. Nevertheless both lithium salts investigated demonstrated high thermal stability in air and an outstanding electrochemical stability window. Additionally, one of the salts i.e. **Salt 1** exhibited a very high cationic conductivity.

4. Experimental

4.1. Commercial products

High molecular weight POE, Mw = 5.10^6 g mol⁻¹ was purchased from Janssen. Acetonitrile from Acros Organics was further dried over an activated molecular sieves (3 Å) before use (<15 ppm H₂O) and stored in a glove box.

4.2. Salt syntheses and characterizations

4.2.1. General procedures

All non-aqueous reactions were performed using oven-dried glassware under an atmosphere of argon. Standard inert atmosphere techniques were used in handling all air and moisture sensitive reagents. THF was freshly distilled from sodium benzophenone ketyl. Unless otherwise stated, reagents were purchased from chemical companies and used without prior purification. For chromatographic purification, reagent grade solvents were used as received. Product purification by flash chromatography was performed using Merck Geduran SI60 Silica Gel 60 M (230-400 mesh). Mass spectrometry (LRMS) was recorded on a ThermoFinnigan Mat 95xL apparatus (mode of ionization: electrospray, chemical ionization or electron impact). Melting points were determined with a Büchi apparatus and are given uncorrected. Reactions were monitored by thin layer chromatography (TLC) using aluminiumbacked silica gel plates (Merck, Kieselgel 60 F254). TLC spots were viewed under ultraviolet light. ¹H NMR (300 MHz), ¹⁹F NMR (282 MHz) and ¹³C NMR (75 MHz) spectra were run on a Bruker Advance300 spectrometer, and obtained using CDCl₃ or acetone-D₆. Chemical shifts (δ) are given in ppm vs. TMS (¹H, ¹³C) or CFCl₃ (¹⁹F), used as internal references. Coupling constants / are reported in hertz (Hz). The substitution pattern of the different carbons were determined by a "DEPT135" sequence. Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet,tt = triplet of triplet, br = broad.

N-benzyl-sulfonimide 3. First step: To a solution of anhydrous 1,2-dichloroethane (C = 0.2 M) and sulfonyl fluoride (1 equiv.), under inert atmosphere, was added freshly distilled benzylamine (5 equiv.). The mixture was stirred at 50 °C during 20 h and was followed by TLC and ¹⁹F NMR until sulfonyl fluoride completely disappeared. At room temperature, an aqueous HCl solution (10%) was added, and the mixture was extracted with dichloromethane. The organic phases were dried over MgSO₄, filtered and evaporated. The residue was purified by column chromatography on silica gel with gradient eluent (Pentane/AcOEt 1/0 to 4/1) to obtain a benzyl sulfonamide.

Second step: To a solution of dichloromethane (C = 0.2 M) and benzyl sulfonamide (1 equiv.), under inert atmosphere, was added DIEA (1 equiv.). Then triflic anhydride (1.5 equiv.) was added at

0 °C, the mixture was stirred for 30 min at constant temperature then 1 h at room temperature (followed by TLC and ¹⁹F NMR). Then the products were evaporated, and the residue was dissolved in hot pentane and the supernatant was isolated. The solvent was evaporated and the benzyl sulfonimide was obtained.

N-*Benzyl*-difluoro-(phenylsulfanyl)-*N*-trifluoromethanesulfonylmethanesulfonimide. Precursor of **Salt 1**. Yield = 89%. White solid, mp = 80–84 °C. $C_{15}H_{12}F_5NO_4S_3$. *M* = 461.45 g mol⁻¹. ¹⁹F NMR δ -72.59 (s, 2F), -72.96 (s, 3F). ¹H NMR δ 5.03 (s, 2H, H₇) 7.34–7.56 (m, 8H, H_{Ar}), 7.69 (d, 2H, ³J_{H₂-H₃} = 7.3 Hz, H₃). ¹³C NMR δ 56.3 (s, C₇), 119.0 (q, ¹J_{C-F} = 324.9 Hz, CF₃), 122.4 (t, ³J_{C-F} = 3.0 Hz, C_{Ar4}), 128.8 (s, C_{Ar}), 128.9 (t, ¹J_{C-F} = 327.9 Hz, CF₂), 129.5 (s, C_{Ar}), 129.7 (s, C_{Ar}), 130.0 (s, C_{Ar}), 131.7 (s, C_{Ar}), 132.7 (s, C_{Ar8}), 137.4 (t, ⁴J_{C-F} = 1.1 Hz, C_{Ar3}).

N-Benzyl-2-(phenylsulfanyl)-1,1,2,2-tetrafluoro-N-(trifluoro-methylsulfonyl)-ethanesulfonimide. Precursor of **Salt 2**. Yield = 92%. White solid; mp = 58 °C. C₁₆H₁₂F₇NO₄S₃. *M* = 511.45 g mol⁻¹. ¹⁹F NMR δ –72.82 (s, 3F, CF₃), -85.89 (s br, 2F, SCF₂), -102.85 (s br, 2F, CF₂SO₂N). ¹H NMR δ 5.07 (s, 2H, H₈), 7.37–7.55 (m, 8H, H_{Ar}), 7.65 (d, 2H, ³J_{H2-H3} = 7.4 Hz, H3). ¹³C NMR δ 56.6 (s, C₈), 116.7 (tt, ¹J_{F-C} = 305.2 Hz, ²J_{F-C} = 39.0 Hz, CF₂), 119.1 (q, ¹J_{F-C} = 324.9 Hz, C₇), 122.5 (tt, ¹J_{F-C} = 292.4 Hz, ²J_{F-C} = 31.3 Hz, CF₂), 122.9 (t, ³J_{F-C} = 3.3 Hz, C_{Ar4}), 128.9 (s, C_{Ar}), 129.6 (s, C_{Ar5}), 129.7 (s, C_{Ar7}), 131.4 (s, C_{Ar7}), 132.3 (s, C_{Ar9}), 137.5 (s, C_{Ar3}). (*Trifluoromethyl)-(perfluoroalkyl)sulfonimide lithium*. A solution

(*Trifluoromethyl*)-(*perfluoroalkyl*)sulfonimide lithium. A solution of ethanol (C = 0.2 M) and benzyl sulfonamide (1 equiv.) was stirred at room temperature for 8 h then LiOH·H₂O (1 equiv.) was added. The mixture was stirred overnight and dried evaporated. The residue was dissolved in diethyl ether and filtrated. The filtrate was evaporated and the residue was washed with pentane to obtain the lithium salt. This compound was hygroscopic and the melting point cannot be determinate.

Difluoro-phenylsulfanyl-N-(trifluoromethanesulfonyl)-methanesulfonimide lithium salt. Salt 1. Yield = 85%. White solid. C₈H₅F₅Li-NO₄S₃. *M* = 377.26 g mol⁻¹. ¹⁹F NMR (Acetone-d6) δ –79.00 (s, 2F), –80.08 (s, 3F). ¹H NMR (Acetone-d6) δ 4.55 (s br), 7.41–7.53 (m, 3H, H_{Ar}), 7.65 (m, 2H, H₃). ¹³C NMR (Acetone-d6) δ 121.0 (q, ¹*J*_{C-} F = 321.8 Hz, CF₃), 126.0 (m, C_{Ar4}), 128.7 (t, ¹*J*_{C-F} = 319.4 Hz, CF₂), 130.0 (s, C_{Ar}), 131.1 (s, C_{Ar}), 137.4 (s, C_{Ar}). SM (ESI-MeOH) *m*/ *z* = 370.0 (M⁻, 100%), 371.0 [(M+1)⁻, 12%], 372.0 [(M+2)⁻, 12%], 746.8 [(2M+Li)⁻, 55%], 746.8 [(2M+1 + Li)⁻, 10%], 746.8 [(2M+2 + Li)⁻, 10%], 762.7 [(2M+Na)⁻, 12%]. SMHR calcd for C₈H₅F₅NO₄S₃: 369.9301; found: 369.9306.

2-(Phenylsulfanyl)-1,1,2,2-tetrafluoro-N-(trifluoromethylsulfonyl)-ethanesulfonimide lithium salt. **Salt 2**. Yield = 90%. White solid. C₉H₅F₇LiNO₄S₃. *M* = 427.27 g mol⁻¹. ¹⁹F NMR (Acetone-d6) δ -80.29 (s, 3F, CF₃), -84.94 (t, 2F, SCF₂, ³J_{F-F} = 5.7 Hz), -112.04 (t, 2F, CF₂SO₂N, ³J_{F-F} = 5.7 Hz). ¹H NMR (Acetone-d6) δ 3.43 (s br), 7.46–7.58 (m, 3H, H_{Ar}), 7.69 (m, 2H, H₃). ¹³C NMR (Acetone-d6) δ 115.1 (tt, ¹J_{F-C} = 293.1 Hz, ²J_{F-C} = 34.4 Hz, CF₂), 120.6 (q, ¹J_{F-C} = 321.5 Hz, CF₃), 124.0 (tt, ¹J_{F-C} = 290.4 Hz, ²J_{F-C} = 32.5 Hz, CF₃), 124.4 (m, C_{Ar4}), 130.2 (s, C_{Ar}), 131.6 (s, C_{Ar}), 137.9 (s, C_{Ar3}). SM (ESI-MeOH) *m*/*z* = 420.0 (M⁻, 100%), 421.0 [(M+1)⁻, 10%], 422.0 [(M+2)⁻, 10%], 846.7 [(2M+Li)⁻, 62%], 862.7 [(2M+Na)⁻, 20%]. SMHR calcd for C₉H₅F₇NO₄S₃: 419.9269; found: 419.9266.

4.3. Film processing

The electrolytes were prepared in a glove box by dissolving both POE and the salt in acetonitrile. The resulting solutions were then stirred overnight and casted on a Teflon plate. Solvent evaporation was carried out in a glove box for 18 hrs. The films were then dried under vacuum at 80 °C for 48 hrs and stored in a glove box under argon.

The lithium salt concentration in the film is indicated by the number n = O/Li, which corresponds to the oxyethylene/lithium molar ratio.

4.4. Thermal analysis

Glass transition temperatures, T_{g} , and melting temperatures, T_{m} , were measured in nitrogen flow using a TA Instruments DSC 2920 modulated DSC. In a typical procedure, samples were heated to 100 °C and cooled rapidly to -100 °C and, then the samples were heated at 5 °C/min up to 100 °C. The oscillation period was 60 s and amplitude was ± 1 °C. T_{g} and T_{m} were taken as the inflection point of the specific heat increment at the glass-rubber transition and at the onset of the melting peak, respectively. Around 10 mg of sample were placed in a DSC aluminium crucible in a glove box. Thermogravimetric measurements were carried out with a Netzsch STA409 thermal analyzer. A few milligrams of the sample were heated from room temperature up to 400 °C at 5 °C/min under air flow.

4.5. Conductivity measurements

Conductivities were determined by electrochemical impedance spectroscopy using an HP 4192A Impedance Analyser in the frequency range 5 Hz - 13 MHz. The samples were placed between two stainless steel electrodes, under argon, in a Swagelok cell equipped with Teflon joints and measurements were performed from 100 °C to 20 °C. The temperature was equilibrated for 2 h before each measurement.

4.6. Transference numbers

The transference numbers were determined by the method proposed by Vincent et al. [20], namely through a combination of complex impedance and potentiostatic polarization measurements. Symmetrical Li/electrolyte/Li cells were assembled in a glove box in a Swagelok cell. The experiments were carried out at 70 °C. The polarization voltage was kept at 10 mV using a computer-monitored Solartron 1470 battery test unit.

4.7. Cyclic voltammetry

Cyclic voltammetry was performed, using as support electrolyte a 0.1 M solution of $N(Bu)_4PF_6$ in acetonitrile (ACN), a glassy carbon as working electrode, a platinum auxiliary electrode and a saturated calomel electrode as reference. The salts were dissolved in ACN at a concentration ranging between 2 and 4 mmol. The use of ACN allows exploring the stability towards the oxidation up to 5.8 V vs Li/Li⁺. To explore the stability of the salts towards the reduction a 0.1 M solution of N(Et)₄ClO₄ in propylene carbonate was used as a support electrolyte.

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