

## Polymer electrolytes based on new aryl-containing lithium perfluorosulfonates

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### ABSTRACT

The electrochemical performances of a broad family of new perfluorosulfonate lithium salts bearing an aryl substituent have been investigated. They exhibit, in polymer electrolytes based on POE, high cationic transference numbers, and fairly good cationic conductivities. The electrochemical stability window of some of them is compatible with their use in lithium batteries having lithium metal as negative electrode. The versatility of the syntheses will allow modulating their physico-chemical properties.

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## 1. Introduction

In advanced electrochemical energy sources i.e. lithium batteries, supercapacitors, proton exchange membrane fuel cells (PEMFC), the cation is imposed by the application. Thus the cation is  $\text{Li}^+$  in both Li-ion and Li-polymer batteries,  $\text{H}^+$  in both PEMFC and DMFC,  $(\text{R}_4\text{N})^+$  in supercapacitors. The anion selection is therefore decisive for the performances of the electrolytes and, therefore, of the electrochemical energy sources. This selection must take into account the Life Cycle Assessments of the energy sources that include not only the electrochemical performances (conductivity, cationic transference number  $T^+$ , electrochemical stability window) but also the safety (chemical and thermal stability), the recycling issues and the possibility of reuse of the materials.

Dealing with lithium-ion batteries, the salt currently used,  $\text{LiPF}_6$ , provides, despite its chemical instability, good performances but its safety, due to its limited thermal stability, is questionable. This safety aspect is all the more so since crucial for the automotive implementation.

In lithium-polymer batteries, free of any liquid solvent, in which the polymer has a double function i.e. macromolecular solvent and separator,  $\text{LiTFSI} ((\text{CF}_3\text{SO}_2)_2\text{NLi})$  provides the highest conductivities. It however leads to low cationic transference numbers, its  $T^+$  ranging between 0.05 and 0.15 [1,2] according to

the chemical nature of the host polymer. This low  $T^+$  can generate the formation of a salt gradient into the polymer electrolyte that is detrimental to the battery performances. Thus it has been reported by Newman et al. [3] that a  $T^+$  approaching 1 should, by suppressing the formation of a salt gradient, benefit to the battery performances. Additionally, Rosso et al. [4] using the model of Chalzavieil [5] connected the dendrite formation on lithium metal to the anion mobility. A  $T^+$  equal to 1 requires first linking, by a covalent bond, the anion to the polymeric backbone (ionomer) and second preventing the polymeric chain from moving across the electrolyte. The second condition implies that all the polymer's chains have a length higher than the entanglement threshold. We however recently reported that this condition, which is sufficient for ionomers operating below their  $T_g$  (glass transition temperature), as in PEMFC, is insufficient for ionomers having a high segmental mobility and, therefore very low  $T_g$  as the host polymers of Li batteries [6]. The first condition supposes to have available ionic monomers. Although ionic monomers bearing carboxylate or alkyl/aryl sulfonate anions are commercially available they are unable to provide a sufficient dissociation in aprotic solvents. Due to the requirements of lithium batteries, the molecular or macromolecular solvents must be aprotic, and implies selecting, as anions, conjugated bases of strong acids and, in particular, of superacids. The existing anions as triflate ( $\text{CF}_3\text{SO}_3^-$ ) or perfluorosulfonimide ( $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ ) cannot be easily modified. Therefore, we designed new aryl perfluorosulfonyl fluoride synthons [7] that can be easily turned into their perfluorosulfonate [8] and into their perfluorosulfonimide forms [9].

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In the frame of this paper we will report the performances of some new lithium perfluorosulfonate salts dissolved in a macromolecular solvent, namely poly(oxyethylene) homopolymer whose formula is  $(\text{CH}_2\text{CH}_2\text{O})_n$ .

## 2. Results and discussion

### 2.1. Aryl based perfluorosulfonate anions

The general formula of these anions is shown in Fig. 1. In this general formula X can be a sulphur, S, a carbonyl, CO, a sulfoxide, SO, or a sulfone  $\text{SO}_2$  and  $n = 1$  or 2.

### 2.2. Thermal characterizations of the lithium salts

The thermal characterizations were performed both by thermogravimetric analysis (TGA) and by differential scanning calorimetry (DSC).

### 2.3. DSC

The thermal data on the salts are gathered in Table 1. It must be pointed out that exothermic events, which are probably related to degradations, occur at temperature close to the melting temperature of the salts. Due to the high crystallinity of the salts and to

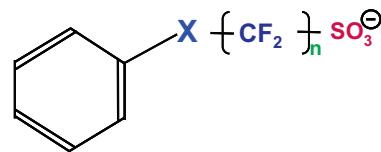


Fig. 1. General formula of the perfluorosulfonate anions.

their fast crystallization after fusion, their glass transition temperature was not detected, excepted for S3.

The DSC measurements were also performed on the polymer electrolytes. These ones were prepared from poly(oxyethylene), POE, host polymer, which is a semi-crystalline polyether whose melting temperature,  $T_m$ , is close to 65 °C. The dissolution of the salts induced, as often observed, a disorder that decreased both the crystallinity ratio and the melting temperature. The melting temperatures of these polymer electrolytes ranged between 35 and 55 °C, depending on the salt and on its concentration. The highest decrease in melting temperatures was observed for POE electrolytes based on S1, which bears a ketone group.

### 2.4. TGA

The thermogravimetric data are gathered in Table 2. TGA analyses show that the thioethers are the less stable salts, the

**Table 1**  
DSC data of the salts.

Salt symbol	Formula	Melting temperature (°C)	Remarks
S1		191	–
S2		187	Onset of an exothermic peak starting around 210 °C
S3		118	A $T_g$ was measured at 64 °C. Onset of an exothermic peak starting around 173 °C
S4		–	No fusion observed before the degradation above 200 °C
S5		–	No fusion observed before the degradation above 200 °C
S6		272	Onset of an exothermic peak starting around 320 °C
S7		226	Onset of an exothermic peak starting around 300 °C

**Table 2**

Thermogravimetric analyses, in air, of the salts.

Salt	Degradation temperature (°C) in air
S1	295
S2	210
S3	210
S4	260
S5	262
S6	371
S7	370

weight loss starting from 210 °C. Following the thioether oxidation, the thermal stability increases. Thus a gain of roughly 50 °C is observed by turning both thioethers into sulfoxides while an outstanding stability is obtained for both sulfones. As for the carbonyl-based salt its thermal stability is intermediary between those of sulfoxides and sulfones. The whole of the salts, exhibit a thermal stability that exceeds considerably the requirements of lithium-polymer batteries.

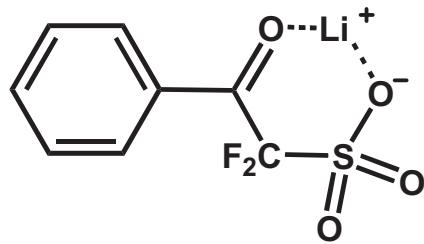
### 2.5. Conductivity measurements

The ionic conductivity of any electrolyte depends both on the concentration in free ions i.e. solvent separated ion pairs and on the ionic mobility. The conductivity dependence on temperature of the polymer electrolytes are compared, at the same concentration O/Li = 20, in Fig. 1.

The whole of the polymer electrolytes exhibited higher conductivities than POE/lithium triflate complexes [10]. The conductivity dependence on temperature follows, as usual in semi-crystalline polymer electrolytes, an Arrhenius law below  $T_m$  and a VTF one above  $T_m$ . The salts providing the highest conductivities were those bearing a thioether group i.e. S2 and S3, with a slight advantage for the latter that reached 0.4 mS/cm at 100 °C. This can be related to the flexibility induced by the thioether function.

The conductivities of POE electrolytes based on the salts bearing a sulfoxide SO or a ketone CO were fairly disappointing. Indeed both groups were expected to increase the electron-withdrawing effect on the anion, thus favouring the salt dissociation. In addition, both are polar groups that should induce, at the vicinity of the salt, an increase in the local permittivity as previously observed for other salts [11]. From these data it might be inferred that both polar groups are involved in an intramolecular chelation of the Lithium cation as shown in Fig. 2.

From theoretical calculations Vandermeeren et al. [12] calculated that the electronegativity of the sulfone group is higher to those of a sulfoxide and, obviously, of a sulphur while, from polycondensation results, Yildiz et al. [13] inferred that the electron-withdrawing effect of a sulfone is higher than that of a ketone. Due to the  $\text{SO}_2$  and to the loss of the flexible thioether moiety, the anions of the salts S6 and S7 are expected to stiffen the POE electrolytes, thus to decrease the ion mobility. Despite the stiffness induced by the sulfone, the conductivity of POE electrolyte based on S6 is however very close to those based on S3 and S2 while S7 leads to slightly lower conductivity. One might assume that, thanks to the electronegativity of its  $\text{SO}_2$  that increases the electron-withdrawing effect, the ion pair dissociation should be favoured, counterbalancing the decrease in ionic mobility. The lower conductivity of POE/S7 might be explained by the fact that an additional  $\text{CF}_2$  is inserted between the sulfonate and the sulfone. This should result in an increased flexibility of the anion but, also, in a decrease in the ion pair dissociation, the electron-withdrawing effect of a  $\text{CF}_2$  being lower than that of a  $\text{SO}_2$ .

**Fig. 2.** Lithium cation chelation.

### 2.6. Transference numbers

The cationic transference numbers,  $T^+$ , were measured, at 70 °C, for several concentrations of the polymer electrolytes. Thereafter the cationic conductivities i.e.  $\sigma^+ = \sigma \cdot T^+$  were calculated. The data are gathered in Table 3.

Most of the salts lead to polymer electrolytes whose  $T^+$  roughly range between 0.4 and 0.55. This must be compared to the  $T^+$  of LiTFSI, determined in the same experimental conditions, which barely exceed 0.1 in the same host polymer [14]. Therefore some cationic conductivities reach 0.1 mS/cm, at O/Li = 20, while, at the same concentration and temperature, the cationic conductivity of POE/LiTFSI is only  $7.5 \times 10^{-5}$  S/cm [14].

### 2.7. Electrochemical stability

The electrochemical stability of an electrolyte is crucial to allow implementing it in a battery. Indeed, an electrochemical instability in reduction or in oxidation can result in interfacial resistances that can markedly exceed the ohmic resistance of the electrolyte. The electrochemical stability of an electrolyte depends both on the salt and on the solvents. The stability in reduction of POE host polymer vs lithium metal is satisfactory while its stability in oxidation is limited at about 3.9 volts vs Li/Li<sup>+</sup>. The electrochemical stability window of the salts was checked by cyclic voltammetry from their solutions in liquid solvents. Additionally POE electrolyte interfaces with lithium metal were investigated.

**Table 3**

Cationic transference numbers and cationic conductivities of the POE electrolytes.

Salt	Concentration	$T^+$	$\sigma$ (70 °C) (S/cm)	$\sigma^+ = \sigma \cdot T^+$ (S/cm)
S1	O/Li = 30	0.49	$8.7 \times 10^{-5}$	$4.3 \times 10^{-5}$
	O/Li = 20	0.41	$9.4 \times 10^{-5}$	$3.8 \times 10^{-5}$
	O/Li = 12	0.44	$5.7 \times 10^{-5}$	$2.5 \times 10^{-5}$
S2	O/Li = 30	0.54	$1.2 \times 10^{-4}$	$6.5 \times 10^{-5}$
	O/Li = 20	0.52	$2 \times 10^{-4}$	$1 \times 10^{-4}$
	O/Li = 12	0.55	$4 \times 10^{-5}$	$2.2 \times 10^{-5}$
S3	O/Li = 30	0.48	$1.8 \times 10^{-4}$	$8.6 \times 10^{-5}$
	O/Li = 20	0.52	$2 \times 10^{-4}$	$1 \times 10^{-4}$
	O/Li = 12	0.47	$8.5 \times 10^{-5}$	$4 \times 10^{-5}$
S4	O/Li = 30	0.39	$1.1 \times 10^{-4}$	$4.5 \times 10^{-5}$
	O/Li = 20	0.39	$9.8 \times 10^{-5}$	$3.8 \times 10^{-5}$
	O/Li = 12	0.43	$6.0 \times 10^{-5}$	$2.6 \times 10^{-5}$
S5	O/Li = 30	0.35	–	–
	O/Li = 20	0.36	$1.1 \times 10^{-4}$	$4.0 \times 10^{-5}$
	O/Li = 12	–	$8.1 \times 10^{-5}$	–
S6	O/Li = 30	0.47	$8.8 \times 10^{-5}$	$4.2 \times 10^{-5}$
	O/Li = 20	0.37	$1.7 \times 10^{-4}$	$6.3 \times 10^{-5}$
	O/Li = 12	0.42	$5.0 \times 10^{-5}$	$2.4 \times 10^{-5}$
S7	O/Li = 30	0.35	$8.6 \times 10^{-5}$	$3.3 \times 10^{-5}$
	O/Li = 20	–	$1.2 \times 10^{-4}$	–
	O/Li = 12	0.41	$1.1 \times 10^{-5}$	$4.5 \times 10^{-6}$

**Table 4**

Cathodic and anodic peaks of the lithium salts. Sweep rate: 200 mV s<sup>-1</sup>, reference: SCE, W.E. glassy carbon, Pt auxiliary electrode. Cyclic voltammetry performed in a support electrolyte NBu<sub>4</sub>PF<sub>6</sub>–acetonitrile.

Lithium sulfonates	Cathodic peak (V vs Li/Li <sup>+</sup> )	Anodic peak (V vs Li/Li <sup>+</sup> )
S1	1.9	>5.8
S2	<0 <sup>a</sup>	5.1
S3	<0 <sup>a</sup>	5.3
S4	0.5	5.6
S5	1.1	5.8
S6	1.5	>5.8
S7	1.5	>5.8

<sup>a</sup> Support electrolyte NEt<sub>4</sub>ClO<sub>4</sub>/propylene carbonate.

### 2.7.1. Cyclic voltammetry

The cyclic voltammetry was performed using 2 support electrolytes. The first one, acetonitrile + NBu<sub>4</sub>PF<sub>6</sub>, is well-adapted to check the stability of the salts in oxidation but unsuitable to explore the stability of the salts at low potentials. The second one was a solution of N(Et)<sub>4</sub>ClO<sub>4</sub> in propylene carbonate. The cathodic and anodic peaks are gathered in Table 4.

The whole of the salts exhibited a high stability in oxidation, which would make them usable in lithium batteries based on high voltage cathodes. The anodic limits of S2 and S3, respectively 5.1 and 5.3 V vs Li/Li<sup>+</sup>, are, despite the presence of a thioether moiety,

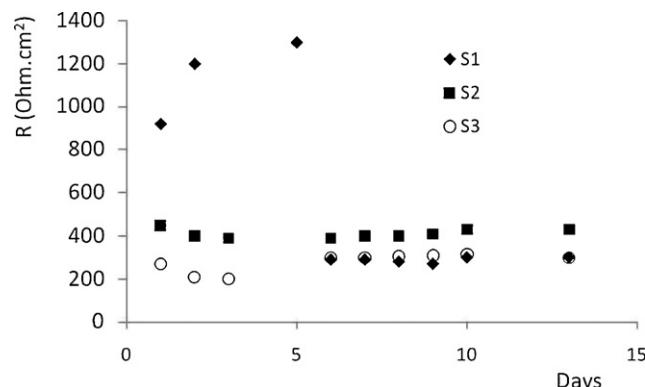


Fig. 4.

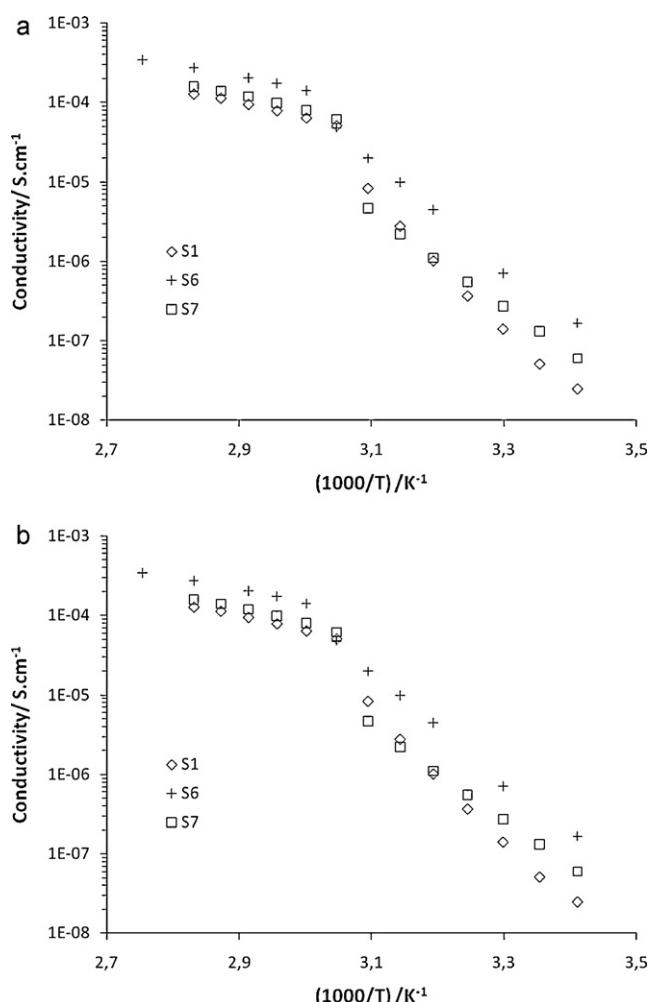


Fig. 3. Arrhenius plots of POE electrolytes made from the new salts.

surprisingly high. This can be ascribed both to a resonance effect involving the sulphur lone pair and the phenyl and to the sulphur substitution by a CF<sub>2</sub>. As the electron-withdrawing effect of the CF<sub>2</sub> is decreased by the sulfonate anion in  $\alpha$  position, S3 that is substituted by two CF<sub>2</sub> is, logically, more stable in oxidation. The anodic stability increases with the degree of oxidation according to SO<sub>2</sub>, CO > SO > S (Fig. 3).

On the contrary the high degrees of oxidation were found detrimental to the cathodic stability. Thus the most stable salts in reduction are the salts including a thioether moiety.

### 2.7.2. Interfacial resistance evolution

The salt concentration, O/Li = 12, of POE electrolytes was selected, despite the fairly low conductivities, to have a high content of salt, potentially unstable, in the membrane. Three salts i.e. S1, S2, S3 were compared. The polymer electrolytes sandwiched between 2 electrodes of lithium metal were heated, for two weeks at 80 °C. The evolutions of the interfacial resistances are compared in Fig. 4.

For the POE electrolytes, based on the salts S2 and S3, the interfacial resistances were found close and stable. On the other hand, after one day POE/S1 electrolyte showed interfacial resistances twice higher than POE/S2 and POE/S3. After one week, the interfacial resistance of POE/S1 still increased by a factor 2, these data being in agreement with the cathodic peak, measured by cyclic voltammetry for S1, at 1.9 V vs Li/Li<sup>+</sup>. Thereafter, the interfacial resistance of POE/S1 strongly decreased to reach the same interfacial resistances than both POE/S2 and POE/S3. This might be ascribed to the formation of a stable passivation film.

### 3. Conclusion

This new family of lithium salts exhibits a high chemical and thermal stability. The conductivities, at ambient temperatures, are insufficient but moving from crystalline POE to amorphous polyether networks will markedly increase them. The cationic transference numbers of these salts, hosted in POE, are much higher than those obtained using the reference salt, LiTFSI. As a result, some of these salts exhibit cationic conductivities close and even higher to those obtained using LiTFSI. S2 and S3 exhibit a good stability in reduction and a wide electrochemical stability window, while S6 and S7 have an outstanding stability in oxidation.

The electrochemical performances, the thermal and chemical stability and the new versatile synthetic routes pave the way for a variety of anions that could be implemented in electrochemical energy sources i.e. PEM Fuel Cells and Batteries.

## 4. Experimental

### 4.1. Products

High molecular weight POE,  $M_w = 5 \times 10^6 \text{ g mol}^{-1}$  was purchased from Janssen. Acetonitrile from Acros Organics was further dried over an activated molecular sieve (3 Å) before use (<15 ppm  $\text{H}_2\text{O}$ ) and stored in a glove box. The syntheses of the salts and their characterizations has been previously described [7,8].

### 4.2. 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 h. The films were then dried under vacuum at 80 °C for 48 h and stored in a glove box under argon.

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

### 4.3. 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. Then the samples were heated at 5 °C/min up to 100 °C. The oscillation period was 60 s and amplitude was  $\pm 1$  °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.

### 4.4. Conductivity measurements

Conductivities were determined by electrochemical impedance spectroscopy using an HP 4192A Impedance Analyser in the frequency range of 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 hours before each measurement.

### 4.5. Transference numbers

The transference numbers were determined by the method proposed by Vincent et al. [15], namely through a combination of complex impedance and potentiostatic polarization measure-

ments. 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.

### 4.6. Cyclic voltammetry

Cyclic voltammetry was performed, using as support electrolyte a 0.1 M solution of  $\text{N}(\text{Bu})_4\text{PF}_6$  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 mM. The use of ACN allows exploring the stability in oxidation up to 5.8 V vs Li/Li<sup>+</sup>. To explore the stability of the salts in reduction a 0.1 M solution of  $\text{N}(\text{Et})_4\text{ClO}_4$  in propylene carbonate was used as a support electrolyte.

### 4.7. Interfacial resistance

The polymer electrolyte was sandwiched between 2 electrodes of Lithium metal in a Swagelok device and heated at 80 °C. By electrochemical impedance spectroscopy it is possible to discriminate between the resistance of the electrolyte and the resistance of the passivation layer formed at the lithium/electrolyte interface.

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