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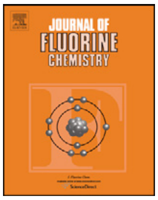

Polymer electrolytes based on new aryl-containing lithium perfluorosulfonates

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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.

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 Li^+ in both Li-ion and Li-polymer batteries, H^+ in both PEMFC and DMFC, $(R_4)N^+$ 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, $LiPF_6$, 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, LiTFSI ($(CF_3SO_2)_2NLi$) 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 Chalzaviel [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 ($CF_3SO_3^-$) or perfluorosulfonimide ($(CF_3SO_2)_2N^-$) 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 $(CH_2–CH_2–O)_n$.

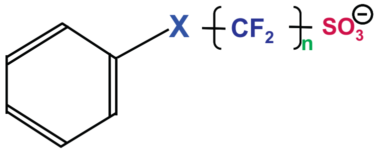


Fig. 1. General formula of the perfluorosulfonate anions.

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 carbonyle, CO, a sulfoxide, SO, or a sulfone 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

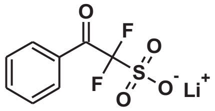
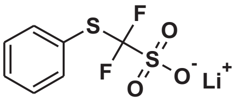
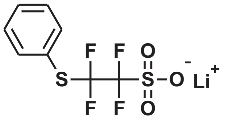
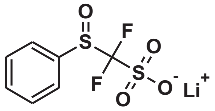
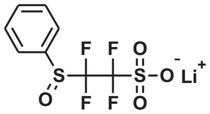
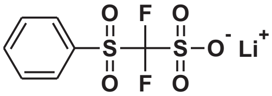
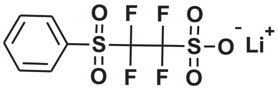
The thermal data on the salts are gathered in Table 1. It must be pointed out that exothermic events, which are probably related to degradations, occur at temperature close to the melting temperature of the salts. Due to the high crystallinity of the salts and to their fast crystallization after fusion, their glass transition temperature was not detected, excepted for S3.

The DSC measurements where 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