

# New Type of Lithium Poly(polyfluoroalkoxy)sulfonylimides as Salts for PEO-Based Solvent-Free Electrolytes

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**ABSTRACT:** A new type of lithium salts,  $-\text{SO}_2\text{N}(\text{LiSO}_2\text{OCH}_2(\text{CF}_2)_n\text{CH}_2\text{O})_m-$  (LiPPFASI, where  $n = 2, 3, 4, 6,$  and  $7$ ), was used as salts in poly(ethylene oxide) (PEO)-based solvent-free electrolytes. The conductivity and electrochemical stability behaviors were studied. The results showed the electrolytes almost have a similar conductivity and the PEO-LiPPFASI ( $n = 3, \text{EO/Li} = 10$ ) was the relatively better system under the experiment conditions. Moreover, most systems were found to be oxidatively stable up to 5.5 V versus  $\text{Li/Li}^+$  and the lithium deposition-stripping process on the electrode was reversible for all the polymer electrolytes. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1882–1885, 2001

**Key words:** fluoropolymers; polyimides; polyethers; blends; electrochemistry

## INTRODUCTION

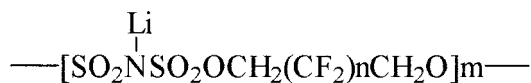
The lithium salts used in solvent-free polymer electrolytes have an important role for conductivity and electrochemical behaviors in the polymer-salt complexes. As a charge carrier, the lithium salts should have the following prerequisites: (i) low ion-ion interaction to obtain a higher percentage of salt dissociation; (ii) plasticizing effect of the anion to reduce the glass transition temperature ( $T_g$ ) of polymer electrolytes and they should eliminate the obstacle for transport of the cation caused by the crystal in the polymer matrix; and (iii) good chemical and electrochemical stability.<sup>1–3</sup> So far, the salts such as  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ , and  $\text{LiAsF}_6$  have been used in polymer electrolytes. However, they still have some disad-

vantages to meet the above requirements. For example,  $\text{LiClO}_4$  can reduce explosions under some conditions.  $\text{LiAsF}_6$  is now regarded as being too toxic for general use, and  $\text{LiPF}_6$  will dissociate into  $\text{LiF}$  and  $\text{PF}_5$  when contacted with lithium metal for a long time.<sup>4</sup>

Recently, the new salts based on perfluoroalkylsulfonylimides and other salts with large anions have been receiving increasing attention due to their special properties. Lithium bis(trifluoromethylsulfonylimide) [ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ , LiTFSI] is a good plasticizer for poly(ethylene oxide) (PEO), and PEO-LiTFSI<sub>0.125</sub> exhibits a high conductivity of  $10^{-5}$  S/cm at room temperature.<sup>5</sup> Nagasubramanian et al. studied electrolytes containing lithium superacid salts of the general formula  $\text{C}_n\text{F}_{2n+1}\text{SO}_3\text{Li}$  ( $n$  is 4, 8, and 10). PEO electrolytes containing  $\text{C}_4\text{F}_9\text{SO}_3\text{Li}$  and  $\text{C}_8\text{F}_{17}\text{SO}_3\text{Li}$  exhibit higher room-temperature conductivity (about  $10^{-6}$  S/cm) compared to those containing  $\text{CF}_3\text{SO}_3\text{Li}$  and  $\text{C}_{10}\text{F}_{21}\text{SO}_3\text{Li}$ .<sup>1</sup> Tominaga and Ohno synthesized  $\text{PEO}_{1000}-(\text{SAMeLi})_2$ , which gave a conductivity of  $10^{-6}$  S/cm at 30°C.<sup>6</sup>

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$n = 2, 3, 4, 6, \text{ and } 7.$

**Scheme 1**

We synthesized a new type of superacid salts, lithium poly(polyfluoroalkoxy)sulfonylimides (Scheme 1), which has a large polymeric anion and exhibited good conductivity in organic solvent electrolytes (about  $10^{-3}$  S/cm, 0.1M lithium salts in 1:2 v/v PC:DME).<sup>7-9</sup> The electrochemical studies of PEO-based electrolytes containing these lithium salts are discussed below.

## EXPERIMENTAL

### Materials

Lithium salts [synthesized by our lab and their mass molecular weights ( $M_w$ ) are 1600, 2600, 2300, 4300, and 3200 for  $n = 2, 3, 4, 6, \text{ and } 7$ , respectively,<sup>8</sup>] were dried at 80°C under a vacuum for 48 h and then kept in a desiccator under a vacuum with  $\text{P}_2\text{O}_5$ . Tetrahydrofuran (THF) was dried over molecular sieves (Type 4A, Merck) for several days before use. PEO ( $M_w = 900,000$ , Acros Organics, Beijing, J & K China Chemical Ltd.) was used as received.

### Sample Preparation

Lithium salts and PEO were each dissolved in THF at 60°C. Then, two solvents were mixed at 60° with magnetic stirring and continuously stirred for 1 h. The solid electrolyte was obtained by completely evaporating THF at room temperature and the remainder was dried under a vacuum at 100°C for 48 h. Finally, the product was heated to 60–70°C in a homemade Teflon mold to acquire a translucent and flexible film (about 500  $\mu\text{M}$  thickness). The film was kept in the desiccator under a vacuum with  $\text{P}_2\text{O}_5$  for the following measurements. All the preparation procedures were carried out in a glove box filled with dry argon.

### Measurements

The conductivity of the electrolytes was measured via an impedance method by sandwiching a given sample between two stainless-steel blocking electrodes (SS, area = 0.5 cm<sup>2</sup>). The measurements

were performed using an SI 1250 frequency response analyzer and an SI 1286 electrochemical interface (Schlumberger Technologies) from 20 to 100°C over a frequency range from 5 to 50 kHz.

The electrochemical stability window was determined by cyclic voltammetry (CV). It was carried out using a three-electrode cell, the stainless-steel block as the working electrode (area = 0.5 cm<sup>2</sup>), a lithium metal disc as the counterelectrode, and a lithium strip interposed between two adjacent layers as the reference electrode. The current-potential curves were recorded by an HB-104 function generator and an HA-501 potentiostat/galvanostat (Hokuto Denko Ltd.) at a 10 mV/s scan rate and a potential range from 0 to 6 V versus Li/Li<sup>+</sup>.

## RESULTS AND DISCUSSION

### Electrolyte Preparation

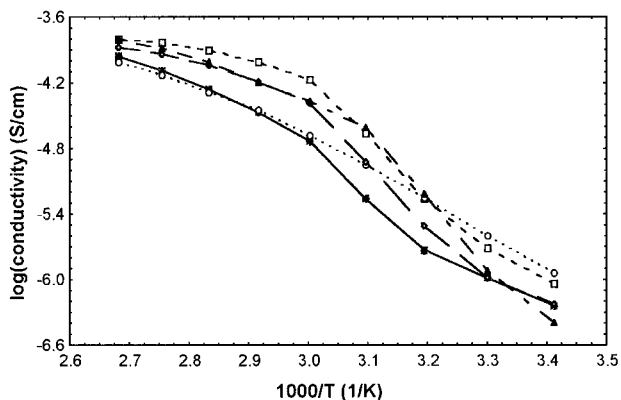
In the preparation of the electrolytes, THF was chosen as the auxiliary solvent because both the salts and PEO were dissolved in it easily and THF could be evaporated completely at room temperature because of its low boiling point (65°C). After a further exsiccate, solvent-free polymer electrolytes were obtained.

The film was obtained by melting the electrolytes at 60–70°C in a homemade Teflon mold. Zhai and coworkers found that the films prepared by the melting method have, obviously, a higher volume specific resistance<sup>10</sup> compared with the complex films prepared by the dissolving method. Also, the thickness of electrolytes could be controlled by this method.

All electrolytes were translucent and flexible films. They have better elasticoviscosity than has PEO at ambient temperature, which suggested that the salts could handicap the forming of crystals in the complexes. These advantages made the electrolytes to have a close contact with the electrodes and to adapt to the volume change of the electrodes during the charge or discharge of the battery.

### Conductivity

For every salt, the most conductive system was obtained by testing the electrolytes with different ratios of oxygen to lithium and the result is discussed below. The Arrhenius conductivity plots exhibited that all the electrolytes were typical

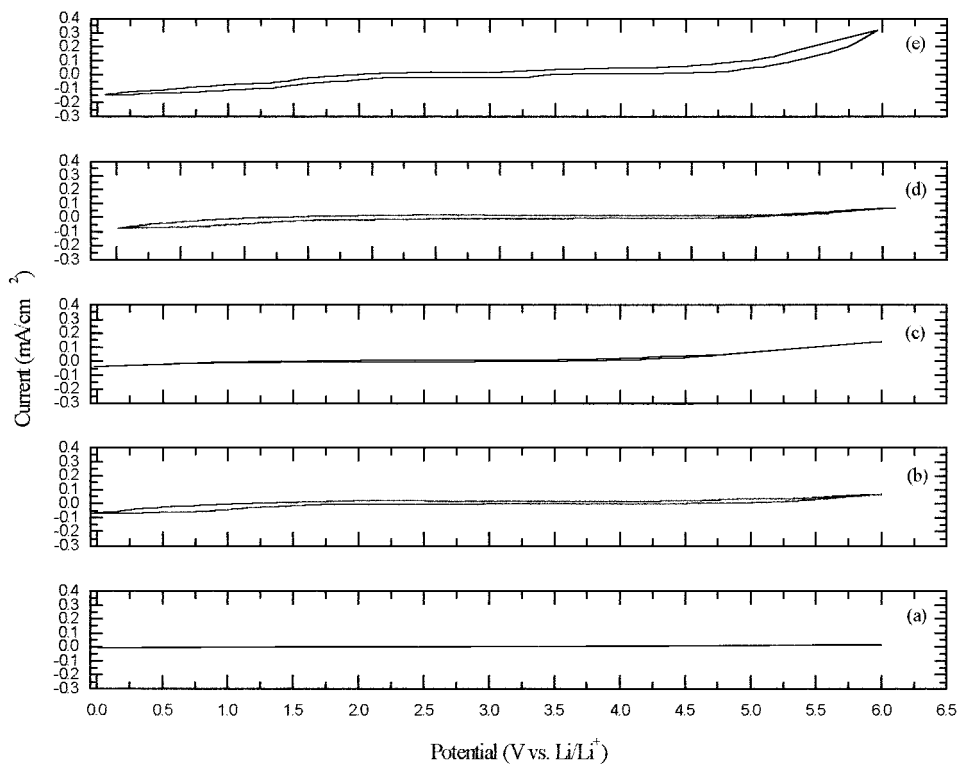


**Figure 1** Temperature dependence of the ionic conductivity for PEO ( $M_w = 900,000$ )-LiPPFASI: (\*) PEO<sub>900,000</sub>-LiPPFASI ( $n = 2$ , EO/Li = 10); (□) PEO<sub>900,000</sub>-LiPPFASI ( $n = 3$ , EO/Li = 10); (○) PEO<sub>900,000</sub>-LiPPFASI ( $n = 6$ , EO/Li = 8); (◇) PEO<sub>900,000</sub>-LiPPFASI ( $n = 4$ , EO/Li = 10); (▲) PEO<sub>900,000</sub>-LiPPFASI ( $n = 7$ , EO/Li = 12).

semicrystalline polymer systems (Fig. 1); the obvious turning point on the plots indicated that there were crystals in the electrolytes, except for

the system PEO<sub>900,000</sub>-LiPPFASI ( $n = 6$ , EO/Li = 8). Up to the turning point, the conductivity increased quickly to above  $10^{-6}$  S/cm because of the melting of the crystals. Under this turning point, the conductivity of electrolytes was below  $10^{-6}$  S/cm, as the crystals of polymer matrix blocked the transportation of lithium ions.

The results showed that the different electrolytes had not only a similar conductivity but also a similar ratio of oxygen to lithium, that is, their salt concentrations were similar (O/Li = 8 or 12), which might be due to their similar dissociative energies of salts as their structures are not obviously different. The salts with  $n = 3$  showed a higher conductivity compared with other salts, namely, there was an extremum of conductivity during the change of the chain's length, which was similar to the result of Nagasubramanian et al.<sup>1</sup> On the other hand, in the case of the PEO-LiPPFASI electrolyte ( $n = 6$ , O/Li = 8), the turning point was not observed, meaning that the salt of LiPPFASI ( $n = 6$ ) has a better hindrance to crystallization and the PEO-LiPPFASI electro-



**Figure 2** CV curve at 50°C of PEO-based electrolytes: (a) PEO-LiPPFASI ( $n = 2$ , EO/Li = 10); (b) PEO-LiPPFASI ( $n = 3$ , EO/Li = 10); (c) PEO-LiPPFASI ( $n = 4$ , EO/Li = 10); (d) PEO-LiPPFASI ( $n = 6$ , EO/Li = 8); (e) PEO-LiPPFASI ( $n = 7$ , EO/Li = 12). Scan rate.: 10 mV/s. Working electrode: SS (0.5 cm<sup>2</sup>).

lyte ( $n = 6$ ,  $O/Li = 8$ ) has the highest room-temperature conductivity under the experiment conditions.

### Electrochemical Stability

The solvent-free polymer electrolytes could optimize the stability of the lithium interface compared with the gel polymer electrolytes. The electrochemical stability of the PEO-LiPPFASI electrolytes was carried out via CV at a 10 mV/s scan rate by sandwiching the polymer electrolytes between a blocking working electrode (SS) and a lithium counterelectrode, plus using a lithium strip as the reference electrode. The anodic and the cathodic voltages at which the current was observed to flow at high values (higher than 0.1 mA/cm<sup>2</sup>) were taken as the breakdown limits of the electrolytes.

Figure 2(a–e) illustrates the CV curves of five categories of PEO-LiPPFASI electrolytes with the best conductivity. One can assume that the anodic breakdown voltage is above 5.5 V versus Li/Li<sup>+</sup> for all samples except for the PEO-LiPPFASI ( $n = 4$ ). Furthermore, the trends of Figure 2(a–e) show that, in all cases, at low voltage (i.e., in the 0 V versus Li region) a cathodic peak is followed by a corresponding anodic peak. This suggests that the lithium deposition-stripping process is reversible for all the polymer electrolytes.

### CONCLUSIONS

A new type of lithium poly(polyfluoroalkoxy)sulfonylimide was used as the charge carrier in PEO-based solvent-free polymer electrolytes and the PEO-LiPPFASI electrolyte ( $n = 6$ ,  $O/Li = 8$ ) has, as a great hindrance to crystallization, the highest room-temperature conductivity under the ex-

perimental conditions. During the preparation of the sample, THF was taken as the auxiliary solvent and the films of the electrolytes were prepared by a dissolving method. The conductivity of the electrolytes is similar at the same temperature and PEO-LiPPFASI ( $n = 3$ ,  $EO/Li = 10$ ) is a better system (above 10<sup>-6</sup> S/cm at ambient temperature). The electrochemical stability windows of the electrolytes were found to be 5.5 V versus Li/Li<sup>+</sup> except for PEO-LiPPFASI ( $n = 4$ ). These noteworthy properties indicate that polymeric lithium salts might be of potential use as a new type of electrolyte for a secondary lithium ion battery or other electronic devices, such as electrochromic windows or ultracapacitors.

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