

# Transport Properties of Solid Polymer Electrolytes Prepared from Oligomeric Fluorosulfonimide Lithium Salts Dissolved in High Molecular Weight Poly(ethylene oxide)

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Transport properties such as ionic conductivity, lithium transference number, and apparent salt diffusion coefficient are reported for solid polymer electrolytes (SPEs) prepared using several oligomeric bis-[(perfluoroalkyl)sulfonyl]imide (fluorosulfonimide) lithium salts dissolved in high molecular weight poly(ethylene oxide) (PEO). The salt series consists of polyanions in which two discrete fluorosulfonimide anions are linked together by [(perfluorobutylene)disulfonyl]imide linker chains. The restricted diffusion technique was used to measure the apparent salt diffusion coefficients in SPEs, and cationic transference numbers were determined using both potentiostatic polarization and electrochemical impedance spectroscopy methods. A general trend of diminished salt diffusion coefficient with increasing anion size was observed and is opposite to the trend observed in ionic conductivity. This unexpected finding is rationalized in terms of the cumulative effects of charge carrier concentration, anion mobility, ion pairing, host plasticization by the anions, and salt phase segregation on the conductivity.

## Introduction

Solid polymer electrolytes (SPEs) containing low lattice-energy lithium salts dissolved in polyether hosts such as poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), poly(ethylene glycol) (PEG), etc. are being actively developed for use in rechargeable lithium ion battery technology. Of all the lithium salts, one might wish to use in such SPEs those based on anions similar to the bis[(trifluoromethyl)sulfonyl]imide (TFSI) anion, called bis[(perfluoroalkyl)sulfonyl]imide (or fluorosulfonimide) lithium salts, which are attractive due to their very low lattice energy and subsequent high degree of dissociation in polyether solvents.<sup>1,2</sup> The combination of PEO and LiTFSI is known to have high ionic conductivity and excellent chemical, thermal, and electrochemical stability, and electrolytes having this composition are good candidates for use in all polymer lithium batteries.<sup>3–6</sup>

Unfortunately, anion motion tends to be the dominant mode of ion transport in these electrolytes,<sup>7,8</sup> which is problematic for batteries since at high power output, the cell can exhibit salt concentration polarization. That is why polyanions are attractive due to the possibility of limited anion motion (predominant cationic conduction is desired in a lithium battery). Also, greater delocalization of the negative charge can be achieved in polymeric anions, which can reduce ion pairing and increase ionic conductivity.

To fully characterize the behavior of a binary salt/polymer electrolyte in an operating cell, it is necessary to know three

transport properties: ionic conductivity, salt diffusion coefficient, and cationic transference number. Several characterization methods for measuring salt diffusion coefficients have been developed that can be classified into perturbing and nonperturbing methods. Perturbing methods such as restricted diffusion are generally based on measuring the response in time during and following the passage of a current, usually under either potentiostatic or galvanostatic control conditions.<sup>9,10</sup> The temporal response can be interpreted using models based on both dilute and concentrated solution theory.<sup>11</sup> This method was recently adapted for studying solid polymer electrolytes.<sup>6,12–14</sup> Nonperturbing methods, such as pulsed-field gradient nuclear magnetic resonance (PFG-NMR), focus on the line width and the relaxation time of ions after applying a nuclear spin gradient.<sup>15–17</sup> Methods used to determine ion transference numbers generally involve creating an electrical potential gradient,<sup>18–22</sup> a chemical potential gradient,<sup>23,24</sup> a radiotracer gradient,<sup>16</sup> or a nuclear spin gradient like in PFG-NMR<sup>23,25</sup> or electrophoretic nuclear magnetic resonance (E-NMR)<sup>26,27</sup> and then analyzing the response in time. In the present study, we will focus on the use of electrochemical impedance spectroscopy (EIS) and DC potentiostatic polarization methods to create electrical and/or chemical potential gradients for transference number measurements, EIS for ionic conductivity measurements, and restricted diffusion technique for apparent salt diffusion coefficient determination.

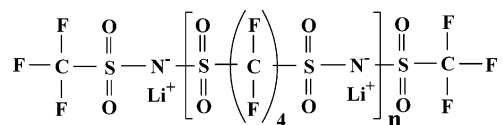
The present study considers SPEs prepared from high molecular weight poly(ethylene oxide) (PEO) and a series of lithium salts based on polyanions with structures similar to that of LiTFSI as illustrated in Scheme 1. The lithium salts were synthesized using methods that have been previously described by DesMarteau and co-workers.<sup>28–31</sup> The polyanion in each of the new salts consists of two terminal fluorosulfonimide units

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**SCHEME 1: Oligomeric Fluorosulfonimide Lithium Salts Used in Solid Polymer Electrolyte Preparation<sup>a</sup>**

<sup>a</sup>  $n = 0$ , LiTFSI;  $n = 1$ , dimer;  $n \approx 5$ , hexamer;  $n \approx 17$ , octadecamer; and  $n \approx 24$ , oligomer.

that are connected together by a polyanionic [(perfluorobutylene)disulfonyl]imide oligomeric chain of variable length. The work focuses mainly on transport properties including ionic conductivity, apparent lithium salt diffusion coefficient, and cationic transference number for SPEs at 90 °C and at a polymer-to-salt ratio of EO/Li = 30:1. Thermal characterization by differential scanning calorimetry (DSC) was also pursued to aid in interpreting variable-temperature ionic conductivity data via VTF fitting.

**Experimental Procedures**

**Solid Polymer Electrolyte Preparation.** The oligomeric lithium sulfonimide salts were prepared via a step-growth polymerization that used an exact stoichiometry of two difunctional monomers, bis[(perfluoroethylene)sulfonyl]fluoride,  $\text{FSO}_2-(\text{CF}_2)_4-\text{SO}_2\text{F}$ , and sodium bis[(perfluoroethylene)sulfonylimide trimethylsilane],  $(\text{CH}_3)_3\text{Si}(\text{Na})\text{NSO}_2-(\text{CF}_2)_4\text{SO}_2\text{N}(\text{Na})\text{Si}(\text{CH}_3)_3$ , to provide the desired oligomeric salt. All reactions were carried out under rigorously dry conditions until there seemed to be no further conversion as indicated by  $^{19}\text{F}$  NMR, which was used to monitor the reaction progress. Following the initial synthesis, the oligomeric sodium salts were converted to acid form by dissolution in deionized water followed by passage through a Nafion column in acid form. The lithium salts were obtained by redissolution of the acid in deionized water followed by titration at room temperature with a saturated aqueous solution of  $\text{Li}_2\text{CO}_3$  to an end point of 7.10 as detected using a pH meter. Further details are provided in ref 30.

All solid polymer electrolytes were prepared, handled, and characterized in an argon-filled drybox. The polymeric host, poly(ethylene oxide) (PEO) with an average molecular weight of  $4 \times 10^6$  Da, was supplied by Aldrich. The reference salt, LiTFSI, was provided by the 3M Corporation, and all the oligomeric fluorosulfonimide lithium salts, for which the structures are illustrated in Scheme 1, were synthesized and purified at Clemson using methods that have been described in detail elsewhere.<sup>28–30</sup> Prior to use, both PEO and lithium salts were vacuum-dried for 24–48 h at temperatures of 50–100 °C.<sup>29–32</sup> The lithium ribbon (19 mm wide, 0.75 mm thick) used for capping the stainless steel rod electrodes to prepare non-blocking electrodes was provided by Aldrich.

Free-standing films of polymer electrolytes with a thickness of 100–300  $\mu\text{m}$  were prepared by solvent casting using a  $N,N'$ -dimethylformamide solution (DMF, spectrophotometric grade supplied by ACROS Organics). Details regarding SPE film preparation with different lithium salt concentrations have already been published.<sup>30,32</sup> For the present study, only electrolytes having a lithium salt concentration corresponding to an EO/Li ratio of 30:1 were prepared.

**Measurements.** Thermal properties such as glass transition temperature ( $T_g$ ), the melting temperature of the crystalline region ( $T_m$ ), and the change in molar heat capacity at the glass transition temperature ( $\Delta C_p$ ) were measured for each SPE sample using differential scanning calorimetry (DSC) performed

on a TA Instruments DSC 2920 calorimeter connected, for data analysis, to a TA Instruments Thermal Analyst 3100 workstation.

The complex impedance of all SPEs,  $Z(\omega)$  (expressed in ohms), was measured by EIS, using stainless steel blocking electrodes, as a function of temperature for each SPE film prepared. Impedance spectra were acquired over a frequency range from 10 to  $10^6$  Hz. Each sample was first heated to 120 °C and then slowly cooled to room temperature, and impedance spectra were recorded on the cooling curve in discrete steps every 10 °C until room temperature was reached. The SPE resistance at each temperature was obtained from the complex-plane impedance plot.<sup>21,33,34</sup> The electrolyte ionic conductivity ( $\kappa$ , in units of  $\text{S cm}^{-1}$ ) was calculated using the resistance value as determined from the spike to the real  $Z$  axis, the SPEs thickness (usually 100–300  $\mu\text{m}$ ), and the apparent electrode area. Details regarding all these measurements can be found elsewhere.<sup>30–32</sup>

An EIS method was also employed for cation transference number measurement. Measurements were made using blocking electrodes for the anion and reversible nonblocking electrodes for the lithium cation, so that the experimental cell had the form  $\text{Li}[(\text{polymer})_n\text{LiX}]\text{Li}$ . For this case, the complex impedance spectrum at ambient temperature consisted of three arcs<sup>35,36</sup> that, using the equivalent Randles circuit theory for a SPE with nonblocking electrodes, could be attributed to the various physical/chemical phenomena taking place. The highest frequency semicircle is due to the bulk capacitance of the host polymer ( $C_b$ ) plus the parallel bulk resistance of the electrolyte ( $R_b$ ). At intermediate frequencies, the second arc is associated with the parallel circuit of the double-layer capacitance ( $C_{dl}$ ) and the charge-transfer resistance ( $R_{ct}$ ). At low frequencies, the amount of charge transferred during a half-cycle produces salt concentration gradients in the electrolyte that can be modeled by a Warburg impedance ( $Z_d$ ).<sup>18,37,38</sup> This gives rise to a linear response with a phase angle of approximately 45° in the spectrum that reflects the diffusion-controlled nature of  $Z_d$ .<sup>35,36</sup> At still lower frequencies, the impedance may deviate from the Warburg impedance and return to the real axis (forming a skewed semicircle). This effect may be attributed either to a finite diffusion layer thickness at steady state or to a finite electrolyte thickness.<sup>36</sup> Plotting  $-\text{Im}[Z(\omega)]$  versus  $\text{Re}[Z(\omega)]$ , we obtain from the graphical representation

$$Z(\omega) = R_b + R_{ct} + Z_d \quad (1)$$

These data may be used to calculate cation transference numbers by making assumptions from dilute electrolyte solution theory, which is valid when ion–ion interactions are weak and the electrolyte behaves ideally. Although battery SPEs generally have a high salt concentration with nonideal behavior and strong ionic interactions present, the theory for dilute electrolytes has been used either for its simplicity or, as is the case now, when dealing with relatively low salt concentrations. Under these assumptions, for dilute electrolytes, the cationic transference number becomes<sup>11,35</sup>

$$t_+ = \frac{R_b}{R_b + Z_d} \quad (2)$$

As a general procedure, each sample was heated at 90 °C in an argon-filled drybox and allowed to equilibrate thermally overnight while the lithium–electrolyte interface was stabilized by cycling using a low-frequency low-amplitude AC potential

perturbation. Impedance spectra were then acquired over a frequency range of  $10^{-5}$  to  $10^6$  Hz for each of the electrolytes prepared.

Cationic transference numbers were also obtained using the DC potentiostatic polarization method (also called steady-state current or SSC method), which was originally developed by Bruce and Vincent for ideal solid electrolytes.<sup>22,39,40</sup> A standard symmetric electrochemical cell of the form  $\text{Li}[(\text{Polymer})_n\text{LiX}]\text{Li}$  is polarized by application of a small DC potential, and the resulting current transient is measured. The initial current,  $I_0$ , is considered to be due to migrations of both cation and anion. Because of the cell polarization, the current decreases over time to a steady-state value,  $I_s$ , which is considered to be due to migration of the cation only. Also, the interfacial resistances of the passivating layers (solid electrochemical interface between electrodes and solid polymer electrolyte or SEI) before and after DC polarization are determined by EIS as the initial ( $R_0$ ) and steady-state ( $R_s$ ) resistances. Then, the transference number is calculated using the following equation:

$$t_+ = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \quad (3)$$

The  $\text{Li}^+$  transference numbers ( $t_+$ ) calculated in this way were obtained from measurements made at 90 °C using electrolytes with Teflon mesh embedded. An EG&G Princeton Applied Research 273 potentiostat and an EG&G 5210 lock-in amplifier were used and controlled by the EG&G PowerSuite software.<sup>41</sup>

Restricted diffusion measurements to determine the lithium salt apparent diffusion coefficients ( $D_s$  in units of  $\text{cm}^2/\text{s}$ ) were performed at 90 °C in an argon-filled drybox for each SPE. Symmetrical  $\text{Li}[(\text{polymer})_n\text{LiX}]\text{Li}$  cells containing electrolyte films of known thickness were subjected to galvanostatic polarization at a controlled current density ( $i = 0.5\text{--}2.0$  mA/ $\text{cm}^2$ ) for a short time ( $t_i = 30\text{--}150$  s). Relaxation of the induced open-circuit cell potential ( $\Delta\Phi$ ) back to zero was monitored after the current was turned off. At long times, the potential relaxation follows eq 4, which may be derived from Fick's second law, assuming that the potential difference is proportional to the concentration difference between the two electrode–electrolyte interfaces

$$\ln(\Delta\Phi) = \frac{\pi^2 D_s}{\delta^2} t + A_2 \quad (4)$$

where  $D_s$  is the differential or apparent lithium salt diffusion coefficient ( $\text{cm}^2/\text{s}$ ),  $t$  is the relaxation time (s),  $\delta$  is the film thickness (cm), and  $A_2$  is a constant. The aim of the current interrupt experiments is to establish concentration gradients at the electrode surfaces without allowing the concentration boundary layers to propagate to the center of the cell. To fulfill this requirement, the upper limit for the polarization time ( $t_i$ ) is set by the condition

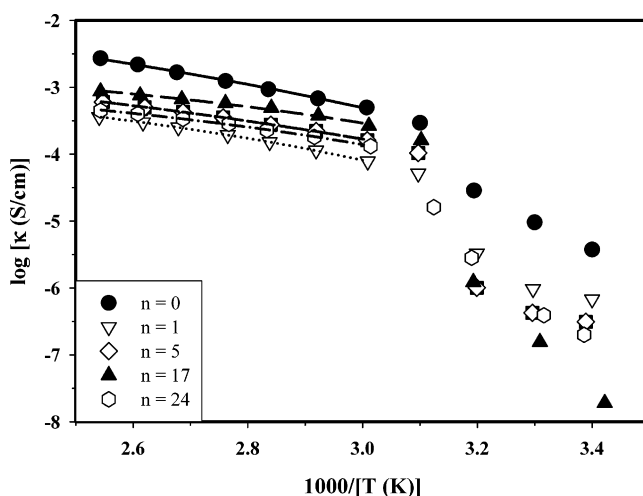
$$t_i \ll \frac{\delta^2}{D_s} \quad (5)$$

We confirmed that for the polarization times, cell thicknesses, and diffusion coefficients in this work, the condition of eq 5 was always met. All of the conductivity and potential relaxation data, and the EIS data from which cation transference numbers were obtained, were collected using a Solartron model SI 1287 electrochemical interface coupled to a Solartron model SI 1260 frequency response analyzer.

**TABLE 1: DSC Characteristics, VTF Parameters, and Apparent Activation Energy of Segmental Polymer Motion ( $\Delta\mu$ ) for Lithium Polyanionic Salts/LiTFSI-Based SPEs Used in This Study (EO/Li = 30:1)**

salt type	$T_g$ (°C)	$T_m$ (°C)	$A$ ( $\text{K}^{1/2} \text{ S/cm}$ )	$B$ (K)	$\Delta\mu \pm \sigma^a$ (kJ/mol)
$n = 0$	−54	59	3.03	808	$15.4 \pm 1.4$
$n = 1$	−29	59	0.14	520	$9.8 \pm 0.9$
$n \approx 5$	−27	67	0.15	437	$8.2 \pm 0.7$
$n \approx 17$	−28	66	0.17	390	$7.3 \pm 0.6$
$n \approx 24$	−25	61	0.23	508	$9.5 \pm 0.6$

<sup>a</sup> Errors corresponding to the standard deviation (SD) calculated from four measurements.



**Figure 1.** Comparison between Arrhenius plots for polymer electrolytes made of LiTFSI or lithium fluorosulfonimide and PEO (the lines represents VTF fits of the data).

## Results and Discussion

**Ionic Conductivity.** The thermal properties for all SPEs prepared using lithium fluorosulfonimide oligomeric salts, such as glass transition temperature ( $T_g$ ) and the melting temperature of the crystalline region ( $T_m$ ) obtained from DSC thermograms, are listed in Table 1. Also, the value for the differential molar heat capacity at the glass transition temperature was calculated and corrected for the salt content of the SPEs ( $\Delta C_p^{\text{corr}} = 11.6 \pm 0.7$  J/mol K). Table 1 also presents a summary of VTF fits to variable-temperature conductivity data (see Figure 1), where the terms  $A$  and  $B$  are phenomenological fitting parameters:<sup>34,42</sup>  $A$  is related to the concentration of charge carriers, and  $B$  is related, in the configurational entropy model, to the apparent activation energy opposing the rearrangement of the polymer segmental unit ( $\Delta\mu$ ).<sup>43,44</sup> Details of the fitting procedure were published earlier.<sup>30–32</sup>

Ionic conductivities for SPEs made from LiTFSI and all of the oligomeric lithium fluorosulfonimide salts from Scheme 1 are presented in the form of Arrhenius plots of ionic conductivity versus reciprocal absolute temperature (Figure 1). From Scheme 1, it may be observed that the difference between the new salts is determined by the number of anionic repeating units of [(perfluorobutylene)disulfonyl]imide linking the two terminal TFSI motifs together. The ionic conductivities at exactly 90 °C were calculated for all SPEs (Table 2), using the VTF equation and parameters  $A$ ,  $B$ , and  $T_g$  from Table 1.

As we have previously reported,<sup>29,30,32</sup> the data in Figure 1 show that SPEs from all the oligomeric fluorosulfonimide lithium salts exhibit conductivities that are lower than that of SPEs prepared using the monolithium salt LiTFSI. The primary



**TABLE 2: Transport Properties Determined at 90 °C for Lithium Polyanionic Salts/LiTFSI-Based SPEs Used in This Study (EO/Li = 30:1)**

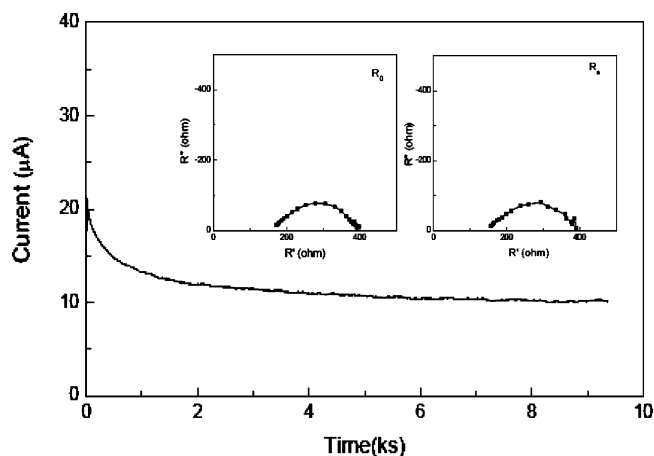
salt type	$D_s \pm \sigma^a$ ( $10^{-8}$ cm <sup>2</sup> /s)	$\kappa$ ( $10^{-3}$ S/cm)	$t_+ \pm \sigma^a$		Li salt concn (wt %)
			SSC	EIS	
$n = 0$	$4.2 \pm 0.8$	1.33	$0.31 \pm 0.02$	0.15	17.9
$n = 1$	$1.9 \pm 0.7$	0.20	$0.37 \pm 0.02$	0.16	19.4
$n \approx 5$	$1.3 \pm 0.3$	0.34	$0.41 \pm 0.03$	0.17	20.5
$n \approx 17$	$0.5 \pm 0.06$	0.58		0.17	20.8
$n \approx 24$		0.28	$0.48 \pm 0.03$		20.8

<sup>a</sup> Errors corresponding to the standard deviation (SD) calculated from three measurements.

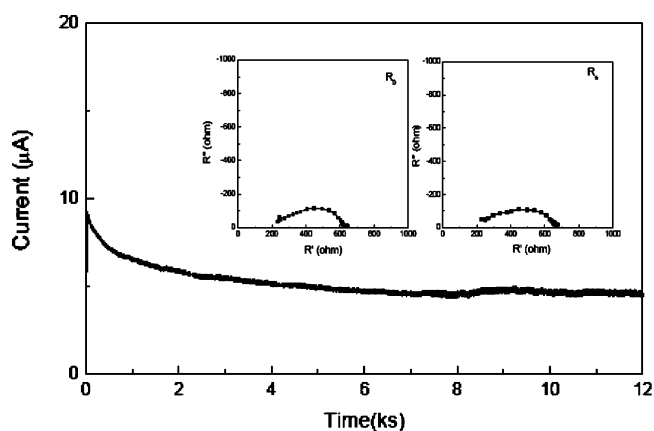
difference among the various salts lies in the  $A$ -values from the VTF fits in Table 1, which are the highest for LiTFSI but are substantially lower for all of the oligomeric fluorosulfonimide lithium salts. The diminished  $A$ -values suggest that the major cause of the decrease in conductivity is that there are fewer mobile charge carriers present in the oligomeric fluorosulfonimide lithium salt SPEs. A secondary effect is that in all of the oligomeric salt SPEs, the  $B$ -term and the apparent activation energy  $\Delta\mu$  from the VTF fits (Table 1) are diminished relative to that for LiTFSI, which may indicate that these oligomers have affected the local microstructure of the host polymer, acting as plasticizers, lowering the apparent activation energy for ion transport. Finally, another important fact in explaining why the LiTFSI-based SPE has the highest ionic conductivity is that all the oligomeric lithium salt-based SPEs examined in this work exhibit higher glass transition temperatures,  $T_g$ , than the LiTFSI-based ones (Table 1).<sup>30</sup>

Comparing the conductivity data for the individual oligomeric lithium salt-based SPEs with respect to the number of anionic repeating units  $n$  in the region between 60 and 120 °C reveals some unexpected trends. With the exception of LiTFSI ( $n = 0$ ) and the  $n \approx 24$  salt, the ionic conductivity increases with increasing  $n$  from  $n = 1$  to  $n \approx 17$ . We believe that this behavior reflects a balance between two competing effects: on one hand, the increase in  $n$  is generating bigger anions with a lower mobility that have a diminished contribution to the overall ionic conductivity, while on the other hand, the greater fluoroalkyl character of the bigger anions provides greater electron withdrawing character on the sulfonimide substituents that provides better charge delocalization, which increases conductivity by reducing ion pairing and increasing the effective number of charge carriers. These observations suggest that the increased SPE conductivity using the salts within the series in Scheme 1 is a consequence of an increase in the number of charge carriers present in the SPEs. In the case of the SPEs made from the salt with  $n \approx 24$ , there is an additional factor of phase segregation (both its degree of crystallinity and its apparent activation energy are higher than those corresponding to  $n \approx 17$  by 20 and 30%, respectively), resulting in salt-rich regions near each individual anion chain with salt-poor regions between them. Ionic conductivity in such a material will be limited by the conductivity between salt-rich domains and is expected to be low relative to that of an otherwise similar SPE that is not phase segregated.

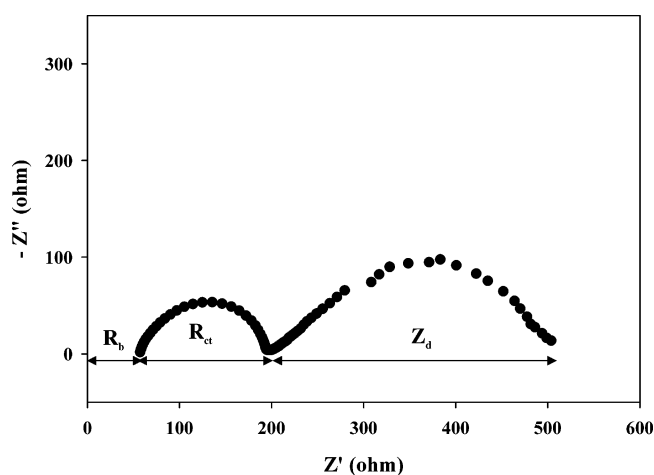
**Cationic Transference Numbers.** Figures 2 and 3 show the current relaxation curves during potentiostatic polarization at a temperature of 90 °C for a PEO/LiTFSI ( $n = 0$ ) and a PEO/hexamer ( $n \approx 5$ ) polymer electrolyte, respectively. The measurements were performed after establishing a stable SEI layer. From these curves, cationic transference numbers ( $t_+$ ) were calculated using eq 3 for all the SPEs prepared and are presented in Table 2. It can be seen that the cationic transference numbers are increasing from 0.31 for LiTFSI to 0.48 for  $n \approx 24$ , which



**Figure 2.** Current relaxation curve during potentiostatic polarization ( $T = 90$  °C,  $V = 10$  mV) for a PEO/LiTFSI ( $n = 0$ ) polymer electrolyte after establishment of a stable SEI layer.



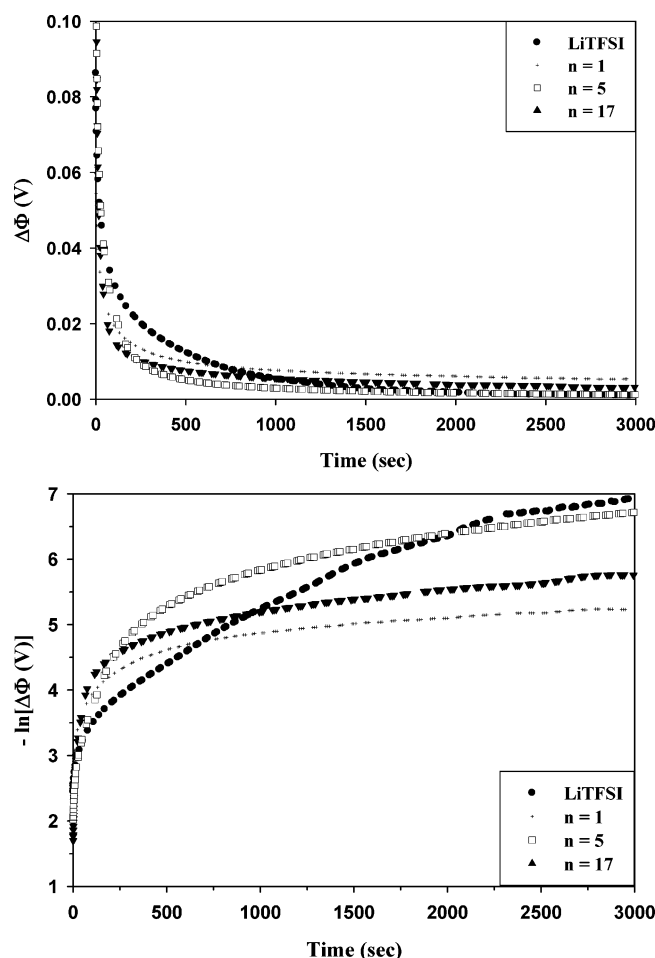
**Figure 3.** Current relaxation curve during potentiostatic polarization ( $T = 90$  °C,  $V = 10$  mV) for a PEO/hexamer ( $n \approx 5$ ) polymer electrolyte after establishment of a stable SEI layer.



**Figure 4.** Complex impedance diagram for a PEO/LiTFSI polymer electrolyte using nonblocking lithium electrodes ( $T = 90$  °C,  $V = 50$  mV,  $f = 10^{-5}$  to  $10^6$  Hz).

was to be expected because increasing the number of anionic repeating units decreases the polyanion contribution to ionic transport. Significantly, the cation transference number never reached unity, which indicates that even for very large and multiply charged anions, there is still an anionic contribution to the overall ionic conductivity.

Figure 4 shows the complex impedance spectrum for a LiTFSI-based polymer electrolyte film in a  $\text{Li}[(\text{polymer})_n\text{LiX}]\text{Li}$



**Figure 5.** Open circuit potential (OCP) relaxation curves after galvanostatic polarization/current interruption for polymer electrolytes containing LiTFSI or an oligomeric fluorosulfonimide and PEO ( $T = 90\text{ }^{\circ}\text{C}$ ,  $i = 1.5\text{ mA/cm}^2$ ).

cell tested at  $90\text{ }^{\circ}\text{C}$ . The spectrum consists only of the intermediate and lower frequency arcs, while the high frequency arc appears to have vanished due to the fact that at temperatures above the melting point of the polymer host (PEO), the capacitive component of the cell impedance is very large and therefore insignificant when in parallel with the other components.<sup>45</sup> From the complex impedance spectra for each of the SPEs prepared, transference numbers ( $t_+$ ) were calculated using eq 2 and are presented in Table 2. From this, it can be seen that the cationic transference numbers increase much more slowly with  $n$ , from 0.15 for  $n = 0$  (LiTFSI) to 0.17 for  $n \approx 17$ .

Generally, the transference numbers determined by the SSC method are systematically higher than those determined by the EIS method. This can be explained by the fact that after reaching the steady-state of migration and back-diffusion, a further small decrease in the measured current proceeds. Therefore, the estimated values of  $t_+$  by the SSC method should be considered as upper limits of the effective transference numbers.<sup>40</sup>

**Apparent Lithium Salt Diffusion Coefficients.** Figure 5 shows open-circuit potential (OCP) relaxation curves acquired after galvanostatic polarization/current interruption for polymer electrolytes containing various oligomeric fluorosulfonimide lithium salts. This figure also shows the data plot in log format: linear fits in the long time scale limit (in this case between 2000 and 3000 s) were used after accounting for the SPE thickness to obtain apparent salt diffusion coefficients, for which values are reported in Table 2.

It is instructive to consider the trends in salt diffusion coefficients with anion structure. For the case of this series, diffusion coefficients varied from  $4.2$  to  $0.5 \times 10^{-8}\text{ cm}^2/\text{s}$  as  $n$  varied between zero and 17. This monotonic decrease in diffusion coefficient with increasing anion size is as expected from a simple Stokes' law model of salt diffusion, whereby diffusion coefficients should scale approximately with the inverse square root of salt molecular weight. Interestingly, as we have reported elsewhere,<sup>30,31</sup> conductivity of dilute acetonitrile solutions of these salts ( $10^{-4}$  to  $10^{-3}\text{ M}$ ) also scales monotonically with the number of fluorosulfonimide repeat units in the oligomeric anion. Such was not the case in the SPEs, where with the exception of the two limiting cases of  $n = 0$  (LiTFSI) and  $n \approx 24$ , the trend in conductivity with anion size is that conductivity increases with increasing  $n$  for values between 1 and 17. As discussed earlier, the reason for this probably relates to variations in the extent of ion pairing and numbers of charge carriers and also to the extent of matrix plasticization caused by the salt anions. These effects are revealed quantitatively in Table 1 via the  $A$ -terms in the VTF fits, which correlate with populations of charge carriers, and the apparent activation energies,  $\Delta\mu$ , which correlate with segmental polymer motions associated with ion motion in the host. As  $n$  increases from 1 to 17, the  $A$ -term is increasing while  $\Delta\mu$  is decreasing, with both factors contributing to increased ionic conductivity.

## Conclusion

A series of solid polymer electrolytes with an EO/Li ratio of 30:1 have been prepared from novel oligomeric fluorosulfonimide lithium salts based on the TFSI anion motif using high molecular weight PEO as the polymer host. The SPE series contained polyanionic lithium salts with the general formula  $\text{CF}_3\text{SO}_2\text{N}(\text{Li})[\text{SO}_2(\text{CF}_2)_4\text{SO}_2\text{N}(\text{Li})]_n\text{SO}_2\text{CF}_3$  where  $n = 0, 1, 5, 17$ , and 24, in which sulfonimide anions are linked together by perfluorobutylene chains. Salt diffusion coefficients obtained using restricted diffusion methods, and cationic transference numbers obtained using both SSC and EIS methods, are reported for SPEs made using each salt. Salt diffusion coefficients exhibit a monotonic decrease with increasing anion chain length  $n$ , a trend that is opposite to the observed trend of increasing ionic conductivity and cationic transference number with increasing  $n$  between 1 and 24. These observations suggest an increased involvement of host plasticization by the larger anions and possibly also of differing degrees of ion pairing for the different chain length salts.

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