Polyether-Based Polymer Electrolytes from New Bis[(perfluoroalkyl)sulfonyl] diimide Dilithium Salts

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INTRODUCTION

Most of the previous work on Li salt-based SPEs has focussed on monoanionic salts, especially $LiClO_4$, LiTFSI, LiTf (1) or lately LiBETI, LiBSMI (2), LiNPSI, etc. (3). In the same time some of the work done involved perfluroalkyl dilithium salts (1, 4) or even polyanionic lithium salts (5-7). The present work considers SPEs prepared from four new lithium salts based on dianions with structures similar to that of LiTFSI (Figure 1), synthesized by DesMarteau and coworkers (6). The dianion in each of the new salts consists of two discrete monoanion units based on LiTFSI motifs that are connected together by a perfluoroalkylene chain of variable length. The polymeric host used was either high molecular PEO or a low molecular weight cross-linked PEG. The work focuses on the ionic conductivity of the SPEs based on the new dilithium salts as a function of temperature.

RESULTS AND DISCUSSION

SPEs preparation (EO/Li=30/1 and 10/1) from the new salts used either a high molecular weight PEO $(4 \cdot 10^6)$ and DMF or low molecular PEG $(2 \cdot 10^3)$ cross-linked with a triisocyanate. The new SPE membranes were free of residual solvent as shown by ^{1}H NMR and MS analyses (8). All of the SPEs studied were characterized, after being used in EIS measurements, by thermal methods and powder X-ray diffraction. As expected, all of the SPEs studied obeyed the VTF semiempirical correlation describing the temperature dependence of conductivity in ionic conductors:

$$\kappa = A \cdot T^{-1/2} \exp[-B/(T-T_0)] \qquad [1]$$

At all temperatures and concentrations the conductivities for SPEs prepared from the new dilithium salts were consistently lower than that of SPEs prepared from monomeric LiTFSI which are probably due to a lower contribution of the dianions to the overall conductivity in the new salt SPEs (Figures 2 and 3). Some unexpected trends in conductivity with respect to anion structure were noted – for PEO-based SPEs and diluted PEG-based (EO/Li=30/1) ionic conductivity increases with the anion size, while for the concentrated PEG-based SPEs (EO/Li=10/1) the trend is the opposite. This behavior suggest that higher conductivities might be achievable in more highly perfluorinated salts. These results are encouraging with respect to application and optimization of polyanionic lithium salts in battery technology.

ACKNOWLEDGEMENTS

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LiTFSI	$R - CF_3$
(1)	$R - (CF_2)_2 - R$
(2)	$R - (CF_2)_4 - R$
(3)	$R - (CF_2)_6 - R$
(4)	$R - (CF_2)_8 - R$

Figure 1. The new lithium salts used in SPEs preparation.
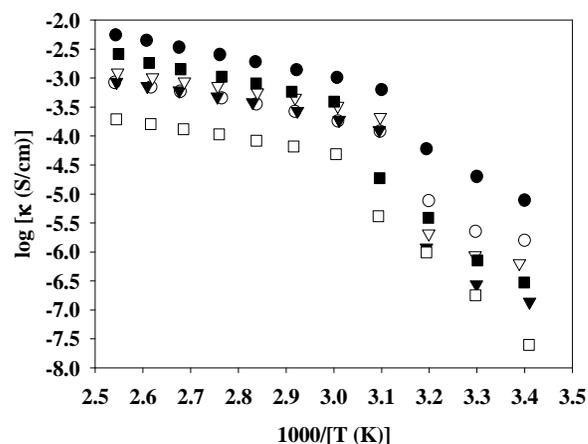
Figure 2. Comparison of Arrhenius plots for SPEs made of PEO and Li salts with EO/Li=10/1: (⌐) LiTFSI; (▤) Salt 1; (▼) Salt 2; (∇) Salt 3; (□) Salt 4.
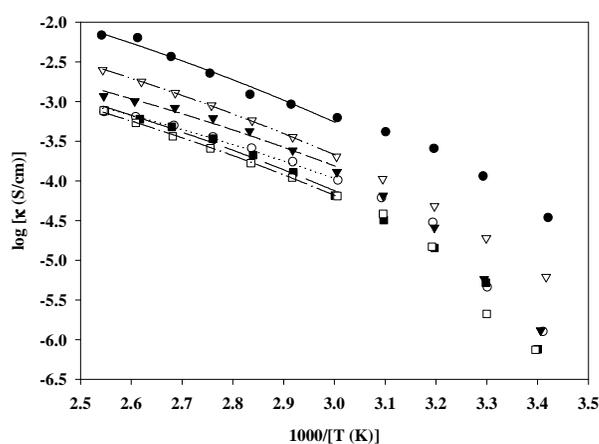
Figure 3. Comparison of Arrhenius plots for SPEs made of cross-linked PEG and Li salts with EO/Li=10/1: (⌐) LiTFSI; (▤) Salt 1; (▼) Salt 2; (∇) Salt 3; (□) Salt 4.