

Solid Polymer Electrolytes from New Lithium Polyanionic Salts Based on LiTFSI Motifs

O.E. Geiculescu, G. Shafer, R. Bailey-Walsh, S.E. Creager, D.D. DesMarteau, W.T. Pennington
Department of Chemistry, Clemson University
H.L. Hunter Laboratory, Clemson, SC 29634-0973

INTRODUCTION

Ion conductivity in solvent-free solid polymer electrolytes (SPEs) has been extensively studied because of their potential applications in electrochemical power sources and devices (1). Most prior work on lithium salt SPEs has focussed on monoanionic salts, especially LiTFSI, LiTf, etc. (1, 2). Lately, some of the work done involved perfluoroalkyl dilithium salts (2, 3). The present work considers SPEs prepared from five new polyolithium salts based on anions with structures similar to that of LiTFSI (Figure 1), synthesized by DesMarteau and coworkers (4). The polyanion in each of the new salts consists of two discrete units based on a LiTFSI motif that are linked to each other by a [(perfluoroalkyl)sulfonyl] imide oligomeric chain. The work focuses on preparation of SPEs from the polyolithium salts in a PEO host (EO/Li=30/1 and 10/1), and on ionic conductivity of the resulting SPEs as a function of temperature.

RESULTS AND DISCUSSION

SPE preparation from the new salts used a high molecular weight PEO as polymer host and dimethylformamide (DMF) as solvent. The new SPE membranes were shown to be free of residual solvent as shown by ¹H NMR and MS analysis and the procedure is described elsewhere (3). All of the SPEs studied were characterized, after being used in EIS measurements, by the DSC and XRD methods. All of the SPEs studied were found to obey the VTF relation describing the temperature dependence of ionic conductivity in ionic conductors:

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

Conductivities for SPEs prepared from the dilithium salts were consistently lower than that of SPEs prepared from monomeric LiTFSI at all temperatures, which probably reflects a diminished contribution of the polyanions to the overall conductivity in the new salt SPEs (Figure 2). This is not necessarily bad since anionic contributions to conductivity are undesirable in battery applications. Some unexpected trends in conductivity with respect to oligomeric chain length were noted which suggest that ionic conductivity is increasing with n, except for the biggest one (n=225) which suggest the existence of a maximum regarding the length of the polyanion. These trends are encouraging with respect to applications of polyanionic lithium salts in battery technology.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support of this research by the DoD (project No. 1910-1400).

REFERENCES

1. F.M. Gray, Solid Polymer Electrolytes: Fundamentals and Technological Applications, VCH, New York (1991).
2. Hongli Dai et al., Abstract 102 at The 199th Meeting of the ECS, Washington, 2001.
3. O.E. Geiculescu et al., Abstract 104 at The 199th Meeting of the ECS, Washington, 2001.
4. D.D. DesMarteau et al., to be published.

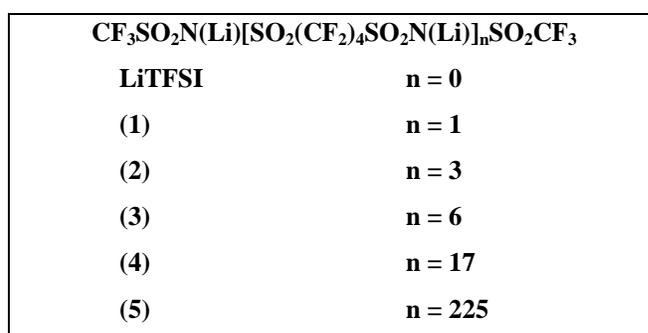


Figure 1. The new lithium salts used in SPEs preparation.

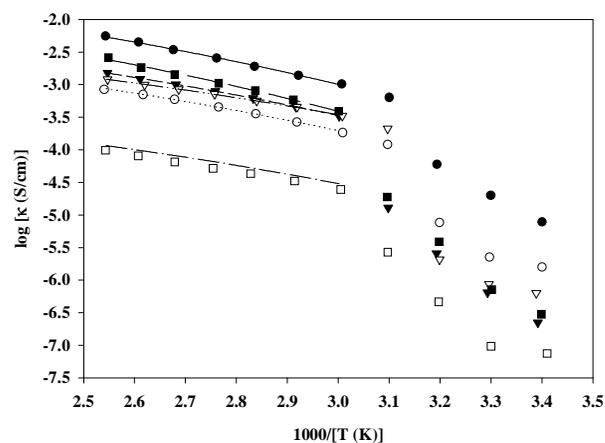


Figure 2. Comparison of Arrhenius plots for SPE membranes made of PEO and Li salts with EO/Li=30/1. Filled circle, LiTFSI; open circle, n=1; filled triangle, n=3; open triangle, n=6; filled square, n=17; open square, n=225.