STUDY OF NOVEL LITHIUM SALT-BASED, PLASTICIZED POLYMER ELECTROLYTES

Maria Manuela Silva^a, Sandra Cerqueira Barros^a, Michael J. Smith^a and James R. MacCallum^b

^a Departamento de Química, Universidade do Minho, 4700-320 Braga, Portugal ^b School of Chemistry, University of St. Andrews, St. Andrews, United Kingdom

Abstract

The results of a preliminary investigation of a series of polymer electrolytes based on a novel polymer host, poly(trimethylene carbonate) or p(TMC), with lithium triflate or lithium perchlorate and various plasticizing additives, are described in this presentation. Electrolytes with lithium salt compositions of about n = 10 (where n represents the molar ratio of $(O=COCH_2CH_2CH_2O)$ units per lithium ion) and additive compositions between 5 and 15 wt% (with respect to p(TMC)), were prepared by co-dissolution of salt and polymer in anhydrous solvent with a controlled amount of additive. The homogeneous solutions obtained were evaporated within a preparative glovebox and under a dry argon atmosphere to form thin films of electrolyte.

The solvent-free electrolyte films produced were characterized by measurements of total ionic conductivity, differential scanning calorimetry and thermogravimetry. In general the triflate-based electrolytes were found to show moderate ionic conductivity and good thermal stability while perchlorate-based electrolytes showed higher levels of conductivity but lower thermal stability. Electrolytes based on this host polymer, with both lithium salts, were obtained as very flexible, transparent, completely amorphous films.

Conclusion

A new host polymer matrix based on polycarbonate rather than polyether coordinating units, with lithium triflate and perchlorate guest species, has been used to prepare plasticized polymer electrolytes. While the conductivity performance of the electrolytes characterized still falls short of that of the best of the amorphous poly(ethylene oxide)-based systems, the use of appropriate quantities of plasticizer has been shown to increase the conductivity of polycarbonate electrolytes to a level which encourages further research into optimization of electrolyte formulation. A better understanding of the polymer-salt-plasticizer interaction may lead to the preparation of electrolytes with suitable properties for practical devices. The results of thermal analysis have confirmed that the new series of polymer electrolytes are completely amorphous. The inclusion of additive in the electrolyte composition allows encouraging levels of conductivity to be achieved at lower salt compositions, relative to the additive-free films. With certain electrolyte compositions the presence of additives also has a useful stabilizing effect on the composite films. The onset of thermal degradation of electrolytes based on lithium perchlorate is however strongly influenced by the amount of salt present in the electrolyte composition. In practical terms this means that a suitable choice of electrolyte composition may provide a useful increase in thermal stability and a significant improvement in the ionic conductivity.

While the polycarbonate electrolytes present adequate mechanical properties, both with and without additives, their ionic conductivity is nevertheless lower than the level which is generally considered appropriate for application in practical devices. Although the total ionic conductivity is certainly one of the most important electrolyte properties, candidate materials must also satisfy various other performance parameters before they can be considered to constitute viable choices for commercial applications. The materials introduced in this presentation are still at a very preliminary stage in their development and further characterization is necessary to determine the extent to which their potential may be realized.

References

- M. B. Armand, J. M. Chabagno, M. J. Duclot, book of abstracts, 2nd International Conference on Solid Electrolytes, St. Andrews, paper 6 (1978) 5.
- [2] J. R. MacCallum, C. A. Vincent (Eds.), Polymer Electrolyte Reviews 1 and 2, Elsevier, London, 1987 and 1989.
- [3] F. M. Gray (Ed.), Solid Polymer Electrolytes: Fundamentals and Technological Applications, VCH Publishers, New York, 1991.
- [4] B. Scrosati (Ed.), Applications of Electroactive Polymers, Chapman and Hall, London, 1993.
- [5] R. G. Linford (Ed.), Electrochemical Science and Technology of Polymers 1 and 2, Elsevier, London, 1987 and 1991.
- [6] F. M. Gray, Polymer Electrolytes, RSC Materials Monographs, Royal Society of Chemistry, London, 1997.
- [7] M. J. Smith, M. M. Silva, S. Cerqueira, J. R. MacCallum, Solid State Ionics 140 (2001) 347.
- [8] C. J. R. Silva, M. J. Smith, Solid State Ionics 40 (1995) 2389.