

Characterization of Lithium-based Solid Polymer Electrolytes

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Sol-gel derived poly(oxyethylene)/siloxane hybrids doped with lithium hexafluoroantimonate, LiSbF_6 , have been prepared. Compositions of these novel xerogel electrolytes were identified using the conventional $\text{d-U}(2000)_n\text{LiSbF}_6$ notation, (where n is the molar ratio of oxyethylene moieties per Li^+ ion) and samples with n between ∞ and 2.5 were characterized by conductivity measurements, cyclic voltammetry at a gold microelectrode and thermal analysis. The electrolyte films produced were obtained as transparent and amorphous monoliths with encouraging electrochemical and thermal properties.

Introduction

The discovery by Wright [1] of polyethylene oxide (PEO / lithium salt complexes, and the subsequent recognition by Armand [2] of the potential application of these materials in a variety of electrochemical devices, has led to a very large number of studies being directed to the elucidation of the properties of this new class of electrolytes. The results of many of these studies have been reviewed [3-6].

Polymer electrolytes are ionically conducting solid phases formed by dissolving salts in ion-coordinating macromolecules. The resulting materials show a range of physical-chemical properties that explain continued interest in this domain both as a possible source of components for technological devices and from an academic point of view [7, 8]. In recent years, the sol-gel method has been successfully used for the production of various novel organic-inorganic frameworks with tunable characteristics [9]. This paper reports the results of a study of a family of sol-gel [9] derived PEO/siloxane hybrid electrolyte materials, designated as di-ureasils, [10, 11] containing a wide range of LiSbF_6 concentration. The di-ureasil matrix is a hybrid structure in which the siliceous framework is bonded through urea bridges to PEO chain segments with about 40 oxyethylene repeat units. The LiSbF_6 – doped di-ureasil samples are represented by the notation $\text{d-U}(2000)_n\text{LiSbF}_6$, where d-U represents the urea bridges at the ends of the PEO chains, 2000 corresponds to the average molecular weight of the organic segment and n indicates the salt composition as molar ratio of OCH_2CH_2 units per cation. The thermal behaviour, ionic conductivity and electrochemical properties of these electrolytes will be discussed in detail.

Previous investigations in our laboratory have demonstrated that these novel organic-inorganic based on different lithium salts [12] have been used as dual-function electrolyte/adhesive components in solid-state electrochromic devices. These materials provide significant advantages in optical performance, cycle lifetime and durability of the electrochromic devices relative to conventional liquid electrolytes.

Experimental

Materials

Lithium hexafluoroantimonate (LiSbF_6), 99%, supplied by Alpha Aesar, was dried under vacuum at 50°C for 10 days and then stored in anhydrous conditions within a dry argon-filled glovebox.

The α , β - diamine poly(oxyethylene-co-oxypropylene) (commercially available from Fluka as Jeffamine ED-2001®, average molecular weight 2001 gmol^{-1}) was dried under vacuum at 25°C for several days prior to use. The bridging agent, 3-isocyanatepropyltriethoxysilane (ICPTES, Aldrich 95 %), was used as received. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, Merck, 99.8%) and tetrahydrofuran (THF, Merck, 99.9%) were dried over molecular sieves. High purity distilled water was used in all experiments.

Sample Preparation

Preparation of the di-ureasil ormolytes

The synthetic procedure used to prepare the LiSbF_6 -based diureasils was based on an optimized two-step method described in detail elsewhere (2). The experimental procedure involves grafting a PEO-based diamine onto the ICPTES substrate to yield the di-urea bridged hybrid precursor. This material was subsequently hydrolyzed and condensed in the sol-gel stage to induce growth of the siloxane network.

Step 1. Synthesis of the di-ureasil precursor, d- UPTES(2000)

2.0 g of Jeffamine ED-2001 were dissolved in 10 ml of THF with stirring. A volume of 0.494 ml of ICPTES was added to this solution in a fume cupboard. The flask was then sealed and the solution stirred for about 12 h at a moderate reaction temperature of approximately 40°C . A urea bridged organic/inorganic hybrid material, designated as di-ureapropyltriethoxysilane (d-UPTES(2000)), was obtained under these conditions.

Step 2. Synthesis of the di-ureasil xerogels, d-U(2000)nLiSbF₆

A volume of 0.467ml of ethanol, an appropriate mass of LiSbF_6 and 0.054ml of water were added to the d-UPTES(2000) solution prepared in the previous step (molar proportion 1 ICPTES:4 $\text{CH}_3\text{CH}_2\text{OH}$:1.5 H_2O). The mixture was stirred in a sealed flask for approximately 30min, cast into a Teflon mould, covered with Parafilm and left in a fume cupboard for 24 h. The mould was transferred to an oven at 50°C and the sample was aged for a period of 4 weeks.

Measurements

Polymer electrolyte sections were removed from dry films and subjected to thermal analysis under a flowing argon atmosphere between -60 and 300°C and at a heating rate of 5°C.min⁻¹ using a Mettler DSC 821e. All samples were presented for analysis in 40 µL aluminium cans with perforated lids to permit the release and removal of decomposition products.

Samples for thermogravimetric studies were prepared in a similar manner, transferred to open platinum crucibles and analyzed using a Rheometric Scientific TG 1000 thermobalance operating under a flowing argon atmosphere. A heating rate of 10°C.min⁻¹ was used to analyze all the electrolyte samples.

Total ionic conductivities of electrolyte samples were determined using a constant volume support (1) with gold blocking electrodes located within a Buchi TO 50 oven. The sample temperature was evaluated by means of a type K thermocouple placed close to the electrolyte film and impedance measurements were carried out at frequencies between 65kHz and 500mHz with a Solartron 1250 FRA and 1286 ECI, over a temperature range of 20 to 100°C. Measurements of conductivity were effected during heating cycles. The reproducibility of recorded conductivities was confirmed by analyzing the results obtained for a sample subjected to two heating-cooling-heating cycles. This procedure demonstrated the correct operation of the support and the mechanical stability of the samples.

Evaluation of the electrochemical stability window of electrolyte compositions was carried out under an argon atmosphere using a two-electrode cell configuration. The preparation of a 25µm diameter gold microelectrode surface, by polishing with a moist cloth and 0.05 µm alumina powder (Buehler), was completed outside the drybox. The microelectrode was then washed with THF (Aldrich, 99.9% inhibitor-free), dried with a hot-air blower and transferred into the drybox. The cell was assembled by locating a freshly-cleaned lithium disk counter electrode (cut from a lithium metal strip, Aldrich, 99.9%, 19mm diameter, 0.75mm thick) on a stainless steel current collector and centering a sample of electrolyte on the electrode surface. A small volume (2µL) of THF was placed on the microelectrode surface. The microelectrode was then located on the electrolyte surface, supported firmly by means of a clamp. The use of THF to soften the electrolyte was necessary to achieve a reproducible microelectrode/electrolyte interfacial contact. An Autolab PGSTAT-12 (Eco Chemie) was used to record voltammograms at a scan rate of 100mV/s. Measurements were performed at room temperature, within a Faraday cage.

Results and Discussion

Thermal behavior of electrolytes

The DSC studies of the d-U(2000)_nLiSbF₆ system are represented in Figure 1. The thermogram of d-U(2000) exhibits a melting peak centered at 40°C*, attributed to the fusion of PEO crystallites, which confirms the semi-crystalline character of this host material (2). The results of thermal analysis confirm that the incorporation of guest lithium salt in the host organic/inorganic matrix produces completely amorphous electrolytes over the entire range of salt concentration studied. The lowest decomposition temperature (203°C) was observed with the n = 20 composition. This hybrid electrolyte

system may therefore be considered to exhibit adequate thermal stability for application in electrochemical devices (Figure 2). At higher salt contents thermal stability increases, a behavior similar to that presented by $d\text{-U}(2000)_n\text{LiClO}_4$ and $d\text{-U}(2000)_n\text{LiTFSI}$ ormolytes (3, 4). The variation of the glass transition temperature over the range of composition of n between 200 and 2.5, observed in this electrolyte system is indicated in Figure 3. It is clear that the value of T_g is proportional to the salt concentration in the electrolytes. As the salt content increases (from high values of n) to higher concentration in salt-rich electrolytes (with low values of n), the T_g of the electrolyte increases. This behaviour has been interpreted as a consequence of a reduction in segmental motion caused by an increase in intramolecular and intermolecular coordinations between Li^+ cations and the oxygen atoms in the polymer chain (5).

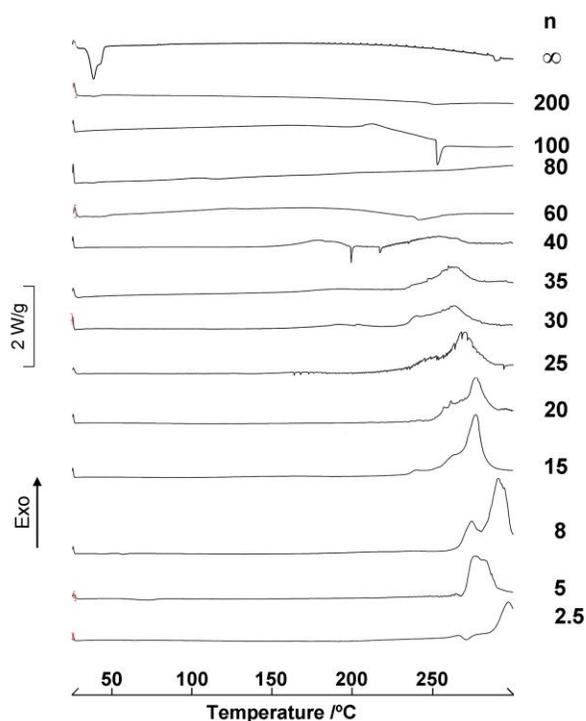


Figure 1. DSC thermograms of selected $d\text{-U}(2000)_n\text{LiSbF}_6$ xerogels.

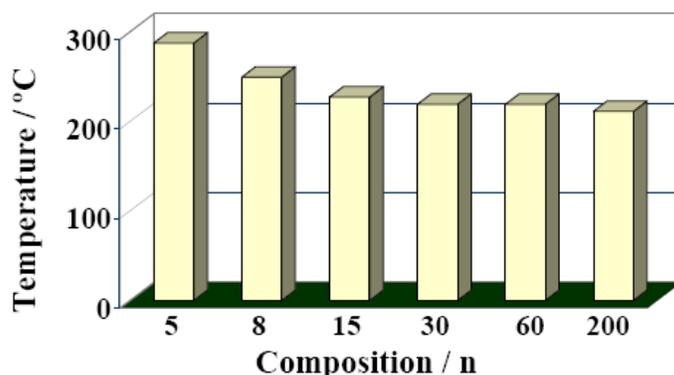


Figure 2. Extrapolated onset of degradation temperatures from TGA characterization of d-U(2000)_nLiSbF₆ xerogels.

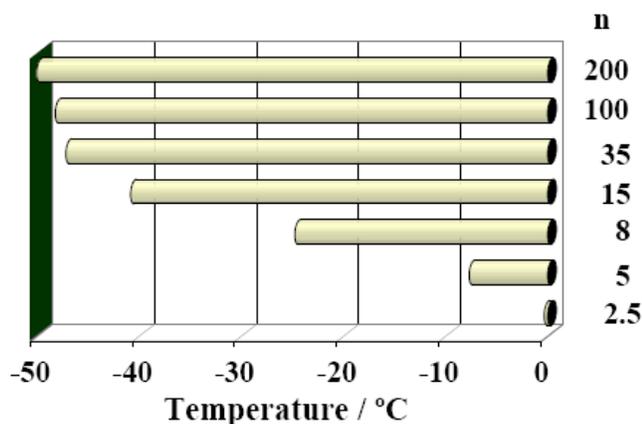


Figure 3. Extrapolated onset* of Glass transition temperatures of d-U(2000)_nLiSbF₆ di-ureasils.

Conductivity Measurements

Figure 4 illustrates the non-linear variation of conductivity with temperature observed in selected compositions of the d-U(2000)_nLiSbF₆ ormolytes. This behavior is typical of polymer electrolytes with predominantly amorphous morphology, an observation consistent with the amorphous character of these xerogels deduced from the DSC data.

The conductivity isotherms, illustrated in Figure 5, confirm that the most conducting di-ureasil sample of the series is U(2000)₃₀LiSbF₆. At room temperature, this xerogel exhibits a conductivity of approximately $1,32 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$. At about 95°C, this electrolyte composition presents the highest conductivity of all the samples investigated ($5,62 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$).

Figure 6 compares the variation of ionic conductivity with temperature of U(2000) di-ureasils doped with different lithium salts. It is clear that at room temperature polymer electrolytes based on LiClO₄ exhibit higher conductivities than those prepared with any other guest salt. At elevated temperatures SPEs based on LiTFSI and LiBF₄ exhibit the highest conductivities ($1.2 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ and $6.49 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$, respectively, at 95 °C) in the temperature range over which electrolytes were characterized.

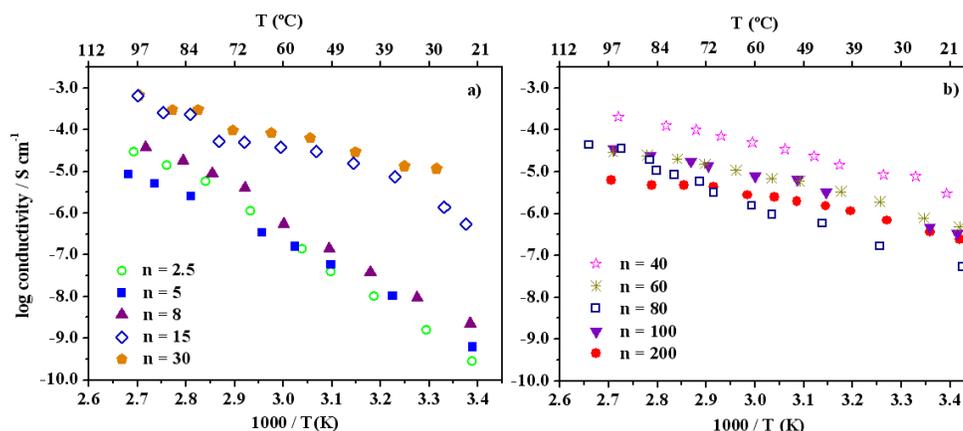


Figure 4. (a and b) Variation of conductivity of selected d-U(2000)_nLiSbF₆ electrolytes with temperature.

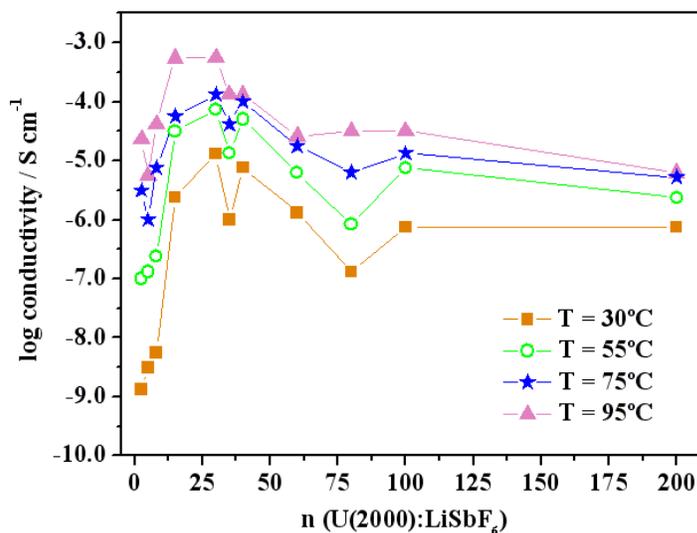


Figure 5. Isothermal variation of ionic conductivity of d-U(2000)_nLiSbF₆ electrolytes

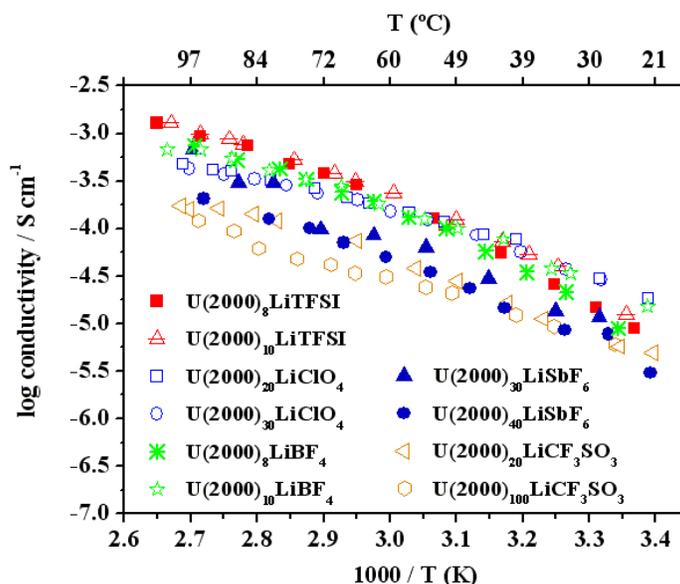


Figure 6. Comparison of ionic conductivity of d-U(2000)_nLiX (X= TFSI, ClO₄, BF₄, SbF₆, CF₃SO₃) electrolytes

Electrochemical stability

The electrochemical stability range of the lithium salt-doped di-ureasils was determined by microelectrode cyclic voltammetry over the potential range -2.0V to 6.0V (Figure 8). The overall stability of electrolytes was excellent, with no electrochemical oxidation occurring at anodic potentials less than about 5V versus Li/Li^+ . These results confirm the applicability of this SPE system in electrochemical devices operating within this range of potentials.

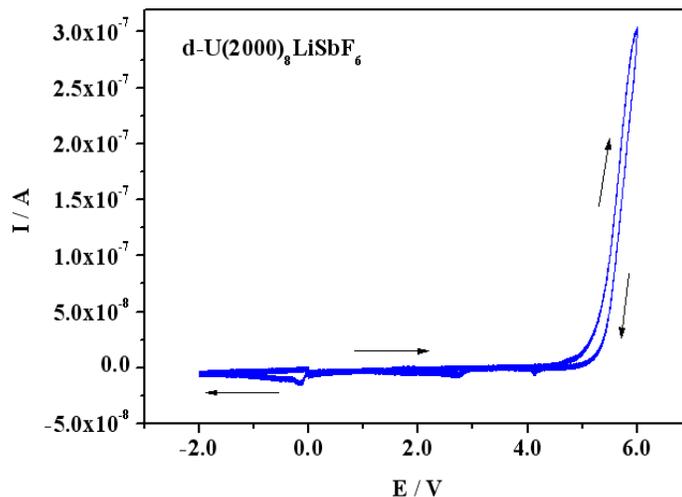


Figure 8. Voltammogram of $d\text{-U}(2000)_8\text{LiSbF}_6$ electrolyte at a $25\mu\text{m}$ diameter gold microelectrode vs. Li/Li^+ . Initial sweep direction is anodic and sweep rate is 100mVs^{-1} .*

Conclusion

The results of conductivity measurements have shown that the di-ureasils system has a similar behaviour to that of other lithium salt-based electrolyte systems. The thermal stability of electrolytes within the composition range of amorphous morphology is sufficient to warrant future investment in the characterization of their optical properties. It seems likely that the most promising application of these polymer electrolytes will be in the domains of electrochromic displays or smart windows.

Preliminary studies of these novel amorphous hybrid networks suggest that exploitation of this approach to the preparation of polymer electrolytes, with the necessary optimization of synthetic conditions and appropriate choice of ionic guest species, may lead to the development of attractive electrolyte components for practical devices.

Acknowledgments

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References

1. P. V. Wright, Br. Polym. J. **7**, 319 (1975).

2. M. B. Armand, J. M. Chabagno and M. J. Duclot, in *Fast Ion Transport in Solids* (Edited by P. Vashishta, J. W. Mundy and F. K. Shenog) Section III, p. 131, Elsevier, Amsterdam (1979).
3. C. A. Vincent, *Prog. Solid State Chem.* **17**, 145 (1987).
4. M. A. Ratner and D. F. Shriver, *Chem. Rev.* **88**, 109 (1988).
5. *Polymer Electrolyte Reviews 2* (Edited by J. R. MacCallum and C. A. Vincent), Elsevier, London (1989).
6. F.M. Gray, *Solid Polymer Electrolytes: Fundamentals and Technological Applications*, VCH, New York, 1991.
7. P. W. Wright, *Electrochim. Acta* **43** 1137 (1998).
8. V. Di Noto, S. Lavina, D. Longo, M. Vidali, *Electrochim. Acta*, **43** 1225 (1998).
9. C. J. Brinker, G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, San Diego CA, 1990.
10. M. Armand, C. Poinignon, J.-Y. Sanchez, V. de Zea Bermudez, US Patent 5, 283,310, 1994.
11. V. de Zea Bermudez, C. Poinignon, M. B. Armand, *J. Mater. Chem.* **7** (9) 1677 (1997).
12. P. C. Barbosa, M. M. Silvaa, M. J. Smith, A. Gonçalves, E. Fortunato, *Electrochimica Acta* **52**, 2938 (2007).
13. M.J. Smith, C.J. Silva, *Portugaliae Electrochimica Acta*, **9**, 225 (1991).
14. S. C. Nunes, V. de Zea Bermudez, D. Ostrovskii, M. M. Silva, S. Barros, M. J. Smith, L. D. Carlos, J. Rocha, E. Morales, *Journal of The Electrochemical Society*, **152**, A429 (2005).
15. M.M. Silva, S.C. Nunes, P.C. Barbosa, A. Evans, V. de Zea Bermudez, M.J. Smith, D. Ostrovskii, *Electrochim. Acta* **52**, 1542 (2006).
16. Paula C. Barbosa, M. Manuela Silvaa, Michael J. Smith, Alexandra Gonçalves, Elvira Fortunato, Sílvia C. Nunes, V. de Zea Bermudez, *Electrochimica Acta* **54**, 1002 (2009).
17. C.A. Angell, K. Xu, S.S. Zhang, N. Videa, *Solid State Ionics* **17**, 86 (1996).