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Cationic and anionic environments in LiTFSI-doped di-ureasils with application in solid-state electrochromic devices

S.C. Nunes [a], V. de Zea Bermudez [a,*], D. Ostrovskii [b], P.C. Barbosa [c], M.M. Silva [c], M.J. Smith [c]

[a] *Departamento de Química and CQ-VR, Universidade de Trás-os-Montes e Alto Douro 5001-801 Vila Real, Portugal*
[b] *Department of Applied Physics, Chalmers University of Technology, 41296 Göteborg, Sweden*
[c] *Departamento de Química, Universidade do Minho, Gualtar, 4710-057 Braga, Portugal*

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Abstract

Fourier Transform mid-infrared and Raman spectroscopies were used to investigate the cation/polymer, cation/urea bridge, cation/anion and hydrogen bonding interactions in poly(oxyethylene) (POE)/siloxane di-ureasil networks prepared by the sol–gel route and doped with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). Materials with compositions $200 \geqslant n \geqslant 5$ (where n expresses the molar ratio OCH_2CH_2/Li^+) were studied. The Li^+ ions coordinate to the urea carbonyl oxygen atoms over the whole range of salt concentration considered. Bonding to the ether oxygen atoms of the POE chains occurs at $n \leqslant 40$, although a significant fraction of the POE chains remain non-coordinated. In these high salt content samples, the cations interact with the anions forming contact ion pairs. "Free" ions are probably the main charge carriers at the room temperature conductivity maximum of these ormolytes.

Keywords: Di-ureasils; LiTFSI; Sol–gel; FT-IR; FT-Raman spectroscopy

1. Introduction

During the last two decades solid polymer electrolytes (SPE) [1] have attracted the attention of many researchers owing to the potential technological impact of these materials in solid-state electrochemistry.

Lithium bis(trifluoromethanesulfonyl)imide ($LiN(SO_2CF_3)_2$, LiTFSI)-based SPE systems [2–6] generally show higher conductivities than other lithium salts [7] in these electrolytes systems. The observed improvement in ionic conductivity has been attributed to the low lattice energy of the salt, which facilitates the solvation of the lithium salt by the polymer, and to the deslocalized negative charge on the nitrogen and four oxygens atoms, which reduces the tendency to form ion pairs. In addition, because of its shape and internal flexibility, the $TFSI^-$ anion exerts a plasticizing effect and reduces the crystallinity of the SPE, therefore lowering the glass transition temperature of the materials.

This paper is devoted to the study of a family of sol–gel [8] derived POE/siloxane hybrid electrolyte materials, designated as *di-ureasils* [9,10], containing a wide range of LiTFSI concentration. The di-ureasil matrix is a hybrid structure in which the siliceous framework is bonded through urea bridges to POE chains with about 40 oxyethylene repeat units. The LiTFSI-doped di-ureasil samples were represented by the notation d-U(2000)$_n$LiTFSI, where d-U represents the urea bridges at the extremes of the POE chains, 2000 corresponds to the average molecular weight of the organic segment precursor and n indicates the salt composition as molar ratio of OCH_2CH_2 units per cation. Studies carried out very recently [11] allowed us to conclude that the d-U(2000)$_n$LiTFSI ormolytes (organically modified silica electrolytes) have potential applications in

* Corresponding author. Tel.: +351 259 350253; fax: +351 259 350480.
E-mail address: vbermude@utad.pt (V. de Zea Bermudez).

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optical devices such as rear-view windows and "smart windows". They exhibit a wide electrochemical stability window of over 5.0 V. Given that in solution the urea molecule is known to undergo anodic oxidation [12,13], the stability observed may initially seem anomalous. In previous studies however, interference of urea on biosensor function has been efficiently blocked by the use of a polymeric layer on the biosensing electrode surface [14]. Stability of a urea linkage group incorporated within a polymer electrolyte network has already been reported in POE/siloxane ormolytes [15,16] and it is likely that this stability arises from an encapsulation/protection effect of the chemical environment of the urea linkage. Spectroscopic data confirmed that at low-to-moderate salt content the ionic guest species coordinate with the carbonyl oxygen atoms of the urea linkages and this may also contribute to the observed electrochemical stability. The d-U(2000)$_n$LiTFSI materials yield higher conductivities than the lithium triflate [15] and lithium perchlorate-based [16] di-ureasil analogues.

In the present paper, we have investigated the local chemical environment of the Li^+ and $TFSI^-$ ions in the d-U(2000) medium with the primary objective of gaining insight into the ionic conductivity mechanism. We note that in the d-U(2000)$_n$LiTFSI ormolytes three coordinating sites are available for the cations. Coordination may occur at the urea carbonyl oxygen atoms (–C═O) and at the polymer ether oxygen atoms (–COC–) provided by the host hybrid framework and at the imide ions of the guest salt. The charge carriers in this type of system may be [7,15–18]: (a) "free" or weakly coordinated ions with high mobility; (b) cations bonded strongly to the host polymer and/or to the urea cross-links with low mobility; (c) ionic aggregates with low-to-moderate mobility.

2. Experimental section

2.1. Materials

Lithium bis(trifluoromethanesulfonyl)imide ($LiN(SO_2CF_3)_2$) was dried under vacuum at 190 °C for 7 days and then stored in a high integrity, dry argon-filled glovebox. The diamine *O*,*O*′-bis(2-aminopropyl) polypropylene glycol-*block*-polyethylene glycol-*block*-polypropylene glycol (commercially available as Jeffamine ED-2001®, Fluka, average molecular weight 2001 g mol^{-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 (CH_3CH_2OH, Merck, 99.8%) and tetrahydrofuran (THF, Merck, 99.9%) were dried over molecular sieves. High purity distilled water was used in all experiments.

2.2. Preparation of the di-ureasil ormolytes

The preliminary stage of the synthesis of the di-ureasils involved the formation of a covalent bond between the terminal NH_2 groups of Jeffamine-2001® ($a + c = 2.5$ and $b = 40.5$) and the –N═C═O group of ICPTES in THF to yield the urea cross-linked organic–inorganic hybrid precursor designated as di-ureapropyltriethoxysilane (d-UPTES(2000)) (molar ratio Jeffamine 2001®: ICPTES = 1:2). The grafting process was infrared monitored. In the second stage of the synthetic procedure, a mixture of CH_3CH_2OH and water was added to the d-UPTES(2000) solution (molar ratio ICPTES:CH_3CH_2OH:H_2O = 1:4:1.5), followed by the incorporation of $LiN(SO_2CF_3)_2$. Samples with $n = \infty$, 200, 100, 80, 60, 35, 25, 10, 8 and 5 were prepared (Scheme 1). The materials were produced as transparent monoliths with a yellowish hue.

2.3. Experimental techniques

2.3.1. Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectra were acquired at room temperature on a Unicam FT-IR spectrophotometer. The spectra were collected over the 4000–400 cm^{-1} range by averaging 120 scans at a wavenumber resolution of 4 cm^{-1}. Solid samples (2 mg) were finely ground, mixed with approximately 175 mg of dried potassium bromide (KBr, Merck, spectroscopic grade) and pressed into pellets.

2.3.2. FT-Raman Spectroscopy

The FT-Raman spectra were recorded with a resolution of 2 cm^{-1} at room temperature with a Bruker IFS-66 spectrometer equipped with a FRA-106 Raman module and a near-infrared continuous YAG laser with wavelength 1064 nm. The spectra were collected over the 3200–300 cm^{-1} range at a resolution of 2 cm^{-1}. The accumulation time for each spectrum was 4 h.

To evaluate complex FT-IR and FT-Raman band envelopes and to identify underlying spectral components, the iterative least-squares curve-fitting procedure in the PeakFit[1] software was used throughout this study. The best fit of the experimental data was obtained by varying the frequency, bandwidth and intensity of the bands and by using Gaussian (FT-IR spectra) and Voight shapes (FT-Raman spectra). A linear baseline correction with a tolerance of 0.2% was employed. The standard errors of the curve-fitting procedure were less than 0.003.

3. Results and discussion

In an attempt to correlate the ionic conductivity data with the extent of ionic association we have examined diagnostic bands of polymer chains, of urea bridges and of the anion which suffer characteristic changes of intensity and/or frequency upon cation coordination.

[1] PeakFit is a product of Jandel Corporation, 2591 Rerner Boulevard, San Rafael, CA 94901, USA.