

Structural studies of novel di-ureasil ormolytes doped with lithium hexafluoroantimonate

L.C. Rodrigues ^a, M. Fernandes ^b, V. de Zea Bermudez ^{b,*}, M.M. Silva ^{a,*}, M.J. Smith ^a

^a Chemistry Research Centre, University of Minho, Gualtar, 4710-057 Braga, Portugal

^b Department of Chemistry and CQ-VR, University of Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal

ARTICLE INFO

Article history:

Received 22 April 2012

Received in revised form 17 July 2012

Accepted 18 July 2012

Available online 8 September 2012

Keywords:

Xerogel

Lithium hexafluoroantimonate

Structure

Complex impedance

ABSTRACT

Hybrid electrolytes produced by the sol–gel process were obtained by doping a di-urea cross-linked POE/siloxane hybrid host framework (d-U(2000)) with lithium hexafluoroantimonate (LiSbF₆). Flexible, transparent xerogel films with $\infty > n \geq 2.5$ (where n , composition, represents the molar ratio of oxyethylene units OCH₂CH₂ per Li⁺ ion), thermally stable to at least 200 °C, were prepared. At 30 °C the highest ionic conductivity of all the electrolytes prepared was $1.32 \times 10^{-5} \text{ S cm}^{-1}$ for $n = 30$. The electrochemical stability windows of these materials span at least 6.0 V. Samples with $n < 200$ are amorphous, homogeneous and non-porous. Crystallites of POE are formed in the most dilute electrolyte ($n = 200$). The guest Li⁺ ions were shown to coordinate to the oxygen atoms of the urea carbonyl groups over the entire range of salt concentration. The great majority of the SbF₆⁻ ions interact with the Li⁺ ions. Contact ion pairs were detected only at $n = 200$. Trace amounts of “free” anions exist in all electrolyte samples.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Since Wright et al. [1] first reported ionic conductivity in complexes formed between linear high molecular weight poly(oxyethylene) (POE) and alkali metal salts, significant progress has been achieved in our understanding of polymer electrolyte (PEs) behavior. These materials have potential application in all-solid-state electrochemical devices, including high-energy density primary and secondary batteries, electrochromic devices (ECDs) and fuel cells [2]. However, as a consequence of the marked tendency of POE-based electrolytes to crystallize and the relatively poor processability of the resulting materials, commercial application of these electrolytes has been delayed. An alternative approach to the preparation of PEs through the sol–gel process [3] leads to the class of oxyethylene/siloxane-based electrolytes. These organic–inorganic hybrid materials are designated by the acronym ormolytes (organically modified silicate electrolytes).

Sol–gel chemistry provides a facile and versatile route to the preparation of amorphous, high-purity, well-controlled organic/inorganic hybrid electrolytes [4] under mild synthetic conditions. Members of this sub-class of electrolytes generally show good thermal and mechanical properties, easy shaping and processability and acceptable room temperature ionic conductivity. Over the past decade, hybrid materials

with foreseeable applications in “smart windows” and reactive labels, sensors, displays and advanced batteries have been developed [5–9].

In the present study di-urea cross-linked oxyethylene/siloxanes doped with lithium hexafluoroantimonate (LiSbF₆) have been investigated. The host matrix of these materials, designated as di-ureasil, was represented by the notation d-U(2000) [10,11]. Electrolyte formulations will henceforth be identified using the conventional notation adopted in the domain of PEs. An electrolyte formulation given as d-U(2000)_nLiSbF₆, indicates that the molar ratio of oxyethylene units OCH₂CH₂ per Li⁺ ion is n [12]. The application of X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Polarized Optical Microscopy (POM), Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) provided information regarding the structure, morphology and thermal behavior of the LiSbF₆-based ormolytes. The ionic conductivity and electrochemical stability domains were determined by means of complex impedance spectroscopy and cyclic voltammetry. On the basis of previous studies carried out on analogous di-ureasils doped with lithium triflate [13], lithium perchlorate [14] and lithium tetrafluoroborate [15], Fourier Transform Infrared (FT-IR) spectroscopic analysis was performed on the d-U(2000)_nLiSbF₆ system in an attempt to elucidate the Li⁺/oxyethylene, Li⁺/urea and Li⁺/SbF₆⁻ interactions and ultimately to clarify the nature and concentration of the species responsible for charge transport.

It must be emphasized that very few studies of PEs incorporating LiSbF₆ have been reported. This compound has been used as a guest salt with POE [16–19], linear poly(ethylenimine) (LPEI) [20] and diglyme [21] host polymers. To the best of our knowledge this salt has never been previously incorporated into a hybrid host network.

* Corresponding author.

E-mail addresses: vbermude@utad.pt (V. de Zea Bermudez), nini@quimica.uminho.pt (M.M. Silva).

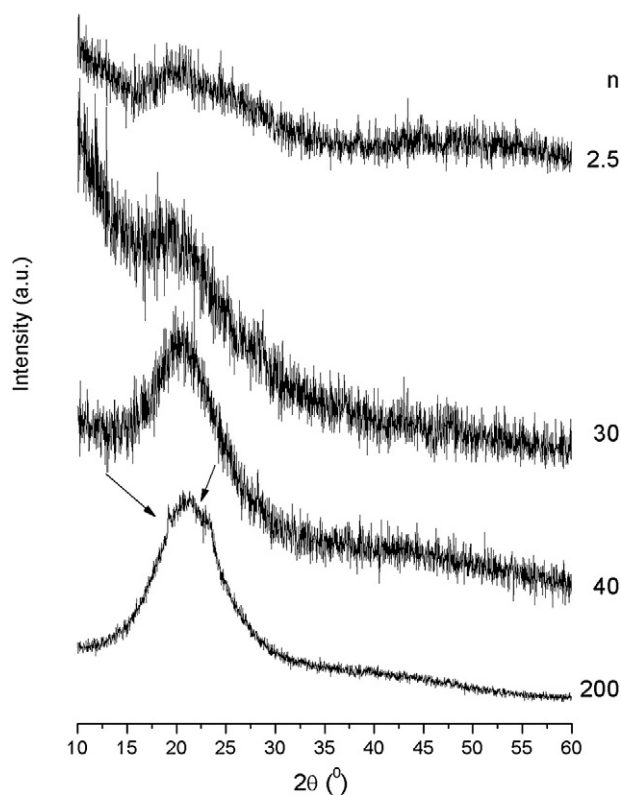


Fig. 1. XRD patterns of selected $d\text{-U}(2000)_n\text{LiSbF}_6$ di-ureasils.

2. Experimental section

2.1. Materials

Lithium hexafluoroantimonate (anhydrous LiSbF_6 , Alpha Aesar 99%) was dried under vacuum at $50\text{ }^\circ\text{C}$ for 10 days and then stored under anhydrous conditions within a high-integrity dry argon-filled glovebox. The α,β -diamine poly(oxyethylene-co-oxypropylene) (Jeffamine ED-2001®, average molecular weight 2001 g mol^{-1} , Fluka) was dried under vacuum at $25\text{ }^\circ\text{C}$ 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.

2.2. Sample preparation

The synthetic procedure used to prepare the LiSbF_6 -based di-ureasils was based on an optimized two-step method described in detail elsewhere [22]. The experimental procedure involved grafting an oxyethylene-based diamine (Jeffamine ED-2001®) onto ICPTES to yield the unhydrolyzed di-urea bridged hybrid precursor ($d\text{-UPTES}(2000)$). This material was subsequently hydrolyzed and condensed in the sol-gel stage to induce the growth of the siloxane network. *Step 1. Synthesis of the di-ureasil precursor, $d\text{-UPTES}(2000)$* : 2.0 g of Jeffamine ED-2001® was 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 was stirred for about 12 h at a moderate reaction temperature of approximately $40\text{ }^\circ\text{C}$. The $d\text{-UPTES}(2000)$ was obtained under these conditions. *Step 2. Synthesis of di-ureasil xerogels, $d\text{-U}(2000)_n\text{LiSbF}_6$* : a volume of 0.467 mL of $\text{CH}_3\text{CH}_2\text{OH}$, an appropriate mass of LiSbF_6 and 0.054 mL, a stoichiometric amount of water, was added to the $d\text{-UPTES}(2000)$ solution prepared in the previous step (molar proportion $\text{ICPTES}:\text{CH}_3\text{CH}_2\text{OH}:\text{H}_2\text{O}=1:4:1.5$). The mixture was stirred in a sealed

flask for approximately 30 min, cast into a Teflon mold, covered with Parafilm and left in a fume cupboard for 24 h. The mold was transferred into an oven at $50\text{ }^\circ\text{C}$ and the sample was aged for a period of 4 weeks. Samples with $n=\infty$ to 2.5 were prepared and obtained as xerogel films with a yellow hue.

2.3. Measurements

XRD patterns were recorded at room temperature using a Philips X'Pert MPD Powder X-ray diffractometer system. The as-prepared ormolyte films were exposed to monochromated $\text{CuK}\alpha$ radiation ($\lambda=1.54\text{ \AA}$) over the 2θ range between 3° and 60° with a 2θ range resolution of 0.02.

In order to evaluate the morphology of the samples, SEM micrographs were obtained using a SEM/ESEM-FEI Quanta 400 scanning electron microscope at high acceleration voltage (20 kV). A small portion of the electrolyte sample was cut, fixed on an aluminum stub with carbon tape and then coated with Au/Pd.

POM images were recorded using an OPTIKA B-600POL microscope equipped with an 8 M pixel Digital Photo Camera. The images were analyzed using with OPTIKA VISION PRO software.

Ormolyte sections were removed from dry xerogel films and analyzed by Differential Scanning Calorimetry (DSC) between -60 and $300\text{ }^\circ\text{C}$ under flowing argon (Ar) atmosphere and at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ using a Mettler DSC 821e. All samples were presented for analysis in $40\text{ }\mu\text{L}$ aluminum cans with perforated lids to permit the release and removal of decomposition products. Samples for TGA studies were prepared in a similar manner, transferred to open platinum crucibles and analyzed at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ using a Rheometric Scientific TG 1000 thermobalance operating under a flowing Ar atmosphere.

The total ionic conductivities of the ormolyte samples were determined using a constant volume support 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 65 kHz and 500 mHz using an Autolab PGSTAT-12 (Eco Chemie), over a temperature range of 20 to $100\text{ }^\circ\text{C}$. Measurements of conductivity were carried out 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 Ar atmosphere using a two-electrode cell configuration. The preparation of a $25\text{ }\mu\text{m}$ diameter gold microelectrode surface, by polishing with a moist cloth and $0.05\text{ }\mu\text{m}$ 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%, 19 mm diameter, 0.75 mm thick) on a stainless steel current collector and centering a sample of ormolyte on the electrode surface. A small volume ($2\text{ }\mu\text{L}$) of THF was placed on the microelectrode surface. The microelectrode was then located on the ormolyte surface, supported firmly by means of a clamp. The use of THF to soften the ormolyte 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 100 mV s^{-1} . Measurements were performed at room temperature, within a Faraday cage located inside a dry argon-filled glovebox.

The FT-IR spectra were acquired at room temperature using a Unicam FT-IR spectrophotometer. The spectra were collected in the $4000\text{--}500\text{ cm}^{-1}$ range by averaging 64 scans at a resolution of 4 cm^{-1} . About 2 mg of each sample was mixed with potassium bromide (KBr, Merck, spectroscopic grade) finely ground and pressed into pellets. The iterative least-squares curve-fitting procedure of PeakFit [23]

Download English Version:

<https://daneshyari.com/en/article/1298173>

Download Persian Version:

<https://daneshyari.com/article/1298173>

[Daneshyari.com](https://daneshyari.com)