

FT-IR and Raman spectroscopic study of di-urea cross-linked poly (oxyethylene)/siloxane ormolytes doped with Zn^{2+} ions

S.C. Nunes^a, V. de Zea Bermudez^{a,*}, D. Ostrovskii^b, L.D. Carlos^c

^aDepartamento de Química and CQ-VR, Universidade de Trás-os-Montes e Alto Douro, 5000-911 Vila Real, Portugal

^bDepartment of Experimental Physics, Chalmers University of Technology, 41296 Göteborg, Sweden

^cDepartamento de Física and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

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Abstract

The interactions occurring in di-urea (–NHC(=O)NH–) cross-linked poly(oxyethylene) (POE)/siloxane hybrids (di-ureasils) doped with zinc triflate ($Zn(CF_3SO_3)_2$) were investigated by Fourier Transform infrared (FT-IR) and Raman (FT-Raman) spectroscopies. Bonding of the Zn^{2+} ions to the urea carbonyl oxygen atoms occurs in the entire range of compositions studied ($\infty > n \geq 1$, where n , salt content, is the molar ratio of oxyethylene moieties per Zn^{2+} ion). At $n > 20$ the incorporation of the guest cations progressively reduces the number of free C=O groups. At $n = 20$ the saturation of the urea cross-links is attained and the Zn^{2+} ions start to coordinate to the POE chains giving rise to the formation of a crystalline POE/ $Zn(CF_3SO_3)_2$ complex. The latter process occurs at the expense of the destruction of the hydrogen-bonded POE/urea structures of the host di-ureasil structure. New hydrogen-bonded associations, more ordered than the urea–urea aggregates present in the non-doped matrix and including $Zn^{2+} \cdots O=C$ coordination, emerge in parallel. “Free” and weakly coordinated $CF_3SO_3^-$ ions, present in all the xerogels studied, appear to be the main charge carriers of the conductivity maximum of this family of ormolytes located at $n = 60$ at 30 °C. In materials with $n \leq 20$ contact ion pairs, “cross-link separated” ions pairs and higher ionic aggregates appear. The data reported demonstrate that the behaviour of the di-ureasils doped with triflate salts depends on the type of cation.

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1. Introduction

Research and development of polymer/salt systems have increased significantly in the past years owing to their foreseen application as electrolytes in solid state electrochemical devices, especially batteries [1]. The most widely used host polymer has been poly(oxyethylene) (POE), as it may dissolve a wide variety of salts. In solid polymer electrolytes (SPEs) the ionic conductivity depends on the nature of the cation and anion, salt concentration and temperature. The charge carriers may be “free” or weakly coordinated ions (high mobility), cations interacting strongly with the host polymer (low mobility) and charged aggregates (moderate to low mobility). An increase in the number of uncharged ion pairs is known to lead to a decrease in the ionic conductivity.

FT-IR and FT-Raman spectroscopies are amongst the most powerful tools available for the elucidation of ion pairing/clustering and polymer complexation in POE-based SPEs, allowing to get insight into the nature and concentration of the species responsible for the charge transport [1]. Such spectroscopic analyses involve the examination of diagnostic bands of the host polymer chains and of the anion that suffer characteristic changes (e.g., frequency shifts or splitting) upon bonding to the guest cations. These studies require the use of an anion whose vibration modes are easily identified in the FT-IR and FT-Raman spectra and whose attribution is well established.

In the present work we will perform a FT-IR and FT-Raman analysis of a series of sol–gel-derived POE-modified siloxane hybrid electrolytes, named di-ureasils [2,3], incorporating a wide concentration range of Zn^{2+} ($\infty > n \geq 1$). The counterion chosen is the triflate ion ($CF_3SO_3^-$), as it is recognized as an excellent ion probe to inspect ionic association. The host di-ureasil matrix employed, represented by the notation d-U(2000) (where d indicates di, U denotes the urea group and 2000

* Corresponding author. Tel.: +351 259 350253; fax: +351 259 350480.

E-mail address: vbermude@utad.pt (V. de Zea Bermudez).

corresponds to the average molecular weight of the starting organic precursor), is composed of a siliceous framework covalently bonded through urea groups to POE chains with about 40.5 repeat units. This implies that the guest cations may be coordinated, not only to the POE ether oxygen atoms and to the CF_3SO_3^- oxygen atoms, as it is the case in the classical POE/ $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ analogue system, but also to the urea carbonyl oxygen atoms.

This paper is the continuation of a recent study devoted to the investigation of the morphology, thermal behaviour and electrochemical properties of $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ -doped di-ureasil ormolytes [4]. To the best of our knowledge this was the first time that the synthesis of Zn^{2+} -doped hybrid electrolytes was reported [4].

Owing to its abundance in nature, non-toxicity, high stability and safe handling in oxygen and humid atmospheres, zinc is an interesting element for the fabrication of rechargeable solid state batteries [5,6]. Electrochemical devices based on zinc yield reasonably high specific and volumetric energy densities. A few SPE systems formed between POE and zinc salts have been proposed [7–11]. Gel polymer electrolytes (GPEs) composed of poly(vinylidene fluoride) (PVDF) [12] or poly(methylmethacrylate) (PMMA) [13], plasticized with polycarbonate and ethylene carbonate and doped with $\text{Zn}(\text{CF}_3\text{SO}_3)_2$, have also been introduced.

Our previous work of the Zn^{2+} -containing di-ureasils [4] allowed us to confirm that the combination of the hybrid concept with the sol–gel strategy allows to successfully overcome the drawbacks associated with POE/salt complexes, in particular the poor processability, a high tendency to form crystalline phases and the occurrence of “salting out” at high guest salt contents. The composites with $n \geq 5$ are entirely amorphous. Only at $n = 1$ was a crystalline POE/ $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ complex of unknown stoichiometry detected [4]. The ionic conductivity of the di-ureasil samples with $100 \geq n \geq 10$ ranges from 3×10^{-8} to $3 \times 10^{-6} \text{ S cm}^{-1}$ at room temperature (RT) (the maximum value was achieved at $n = 60$), whereas the conventional PEO-based electrolytes exhibit conductivities of the order of $10^{-8} \text{ S cm}^{-1}$ [14]. Higher conductivity values were reported for the $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ -doped SPEs of Ikeda et al.’s [11] ($2.1 \times 10^{-4} \text{ S cm}^{-1}$ at RT for a sample containing 4 mol% $\text{Zn}(\text{CF}_3\text{SO}_3)_2$) and the PVDF- and PMMA-based GPEs of Kumar and Sampath ($3.94 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C [12] and $1.3 \times 10^{-3} \text{ S cm}^{-1}$ at 27°C [13], respectively). However, as GPEs are more prone to suffering interfacial problems than ormolytes, the latter materials may be considered more attractive systems in the context of solid state electrochemistry [15].

The primary objective of the RT spectroscopic analysis reported here is to inspect the $\text{Zn}^{2+}/\text{POE}$, $\text{Zn}^{2+}/\text{urea}$ and $\text{Zn}^{2+}/\text{anion}$ interactions in the $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ -based di-ureasil xerogels in an attempt to explain the origin of the ionic conductivity exhibited by the sample with $n = 60$. This FT-IR and FT-Raman spectroscopic examination of the d-U(2000)-based di-ureasils doped with $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ assumes additional interest for two reasons: (1) there are only two papers reported in the literature dealing with the FT-IR signature of POE/ $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ electrolytes [16,17]; (2) it is essential to compare

the spectral signature of the materials investigated in the present work with those reported previously for ormolytes formed between d-U(2000) and lithium [18,19], magnesium [20] and europium [21,22] triflate salts, that exhibit RT ionic conductivities as high as $5.8 \times 10^{-6} \text{ S cm}^{-1}$ at 26°C [18], $4.0 \times 10^{-6} \text{ S cm}^{-1}$ at 35°C [23] and $5.0 \times 10^{-6} \text{ S cm}^{-1}$ at 25°C [21], respectively.

2. Experimental details

2.1. Synthesis

The synthesis of the Zn^{2+} -doped POE/siloxane hybrids is similar to that reported in detail elsewhere for the Eu^{3+} [21,22], Li^+ [18] and Mg^{2+} [23]-based analogues. In accordance with the terminology used in previous papers [18–23], the di-ureasils doped with $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ will be represented henceforth by the d-U(2000) $_n\text{Zn}(\text{CF}_3\text{SO}_3)_2$ notation.

2.2. Experimental techniques

FT-IR spectra were acquired at RT using a Bruker 22 (Vektor) spectrometer placed inside a glove-box with a dry argon atmosphere. The spectra were collected over the $4000\text{--}400 \text{ cm}^{-1}$ range by averaging 150 scans at a spectral resolution of 2 cm^{-1} . Solid samples (2 mg) were finely ground, mixed with approximately 175 mg of dried potassium bromide (Merck, spectroscopic grade) and pressed into pellets. Prior to recording the spectra, the pellets were first vacuum dried at $80\text{--}90^\circ\text{C}$ for about 60 h, in order to reduce the levels of adsorbed water and solvent, and then transferred into a glove-box.

The FT-Raman spectra were recorded at RT with a Bruker IFS-66 spectrometer equipped with a FRA-106 Raman module and a near-infrared YAG laser with wavelength 1064 nm. The spectra were collected over the $3200\text{--}300 \text{ cm}^{-1}$ range at a resolution of 2 cm^{-1} . The accumulation time for each spectrum was 4 h. Baseline correction was performed in all cases.

To evaluate complex band envelopes and to identify underlying spectral components, the iterative least-squares curve-fitting procedure in the PeakFit [24] software was used extensively throughout this study. The best fit of the experimental data was obtained by varying the frequency, bandwidth and intensity of the bands. In the case of the disordered samples with $n \geq 40$ the peaks were fitted using a Gaussian shape; for the more concentrated materials (which contain a crystalline POE/salt phase), we used a Voigt function (a mixed contribution of Lorentzian and Gaussian shapes). 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 the following sections we will examine the FT-IR and FT-Raman spectral signature of the d-U(2000) $_n\text{Zn}(\text{CF}_3\text{SO}_3)_2$ xerogels as a function of salt content in regions sensitive to the cation/POE, cation/urea and cation/anion interactions.

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