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Green polymer electrolytes of chitosan doped with erbium triflate

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ABSTRACT

Green Solid Polymer Electrolytes (SPEs) containing Er^{3+} ions have been prepared by solvent casting process. Chitosan was used as host polymer and the trivalent cations, as erbium triflate ($\text{Er}(\text{CF}_3\text{SO}_3)_3$), have been incorporated into the matrix. The thermogravimetric analysis was used to evaluate the thermal stability of the electrolytes and the minimum onset decomposition temperature was 139 °C. Morphology analysis have revealed the predominant amorphous character of the analysed samples. Complex Impedance Spectroscopy was used to evaluate the conductivity of the samples as a function of temperature. The most conducting electrolyte had higher amount of glycerol ($\text{CS}(\text{ErTrif})_{0.05}\text{Gly}_{0.70}$) and displayed 2.06×10^{-5} and $5.91 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C and 90 °C, respectively. This SPE was chosen to assemble a small electrochromic device with glass/ITO/PB/CS ($\text{ErTrif})_{0.05}\text{Gly}_{0.70}/\text{CeO}_2\text{-TiO}_2/\text{ITO}/\text{glass}$ configuration, which behaviour was studied by cyclic voltammetry and transmittance.

1. Introduction

Over past years, natural polymers have appeared as a promising substitute for synthetic ones [1]. Biopolymers can be used as polymer host in electrolytes and they present very advantages such as low cost, non-toxicity, abundant availability in nature, and environmental and human body compatibility [2]. A variety of natural polymers can be used to prepare SPEs, and starch [3], pectin [4], agar [5], gelatin [6], cellulose [7], and chitosan [8] are only some examples.

Chitosan is a natural low cost biopolymer that can be used as polymer matrix for ionic conduction [9]. It derives from deacetylation of chitin and because of its low cost, biodegradability and non-toxicity it presents promising potential in food industry, cosmetics, and biomedical sectors [10]. Its chemical structure contains anhydroglycose units with amine functional groups, Fig. 1. The aromatic rings help maintaining the thermal stability and the functional groups (hydroxyl and amine) are susceptible to be chemically modified [11]. The lone pair electrons in the functional groups enable the interaction with the added salt [12]. To make chitosan a proton conductor, its powder was dissolved in dilute acetic acid and the resulting solution was left cast until film formation. The obtained films are homogeneous, show high mechanical strength and very low electrical conductivity [13].

In order to overcome the problem with relatively low conductivity of SPEs several approaches have been used. Among some examples suggested in the literature to improve this there are suggested blends of polymers, the addition of ceramic fillers, and use of plasticizers [15].

Plasticization is a very successful process to improve the contact between the electrodes and the electrolytes and to increase the conductivity of the samples because of free volume creation [16]. There are different types of plasticizers that can be used. However, those with small size and high polarity such as glycerol and sorbitol are preferred for use in polymeric systems [17].

On the other hand, it is known that in polymer electrolytes the ionic conductivity has been attributed to amorphous phase and so several approaches should be achieved. Dissolving inorganic acids or salts in a suitable polymer matrix is one way to obtain the amorphous phase [18]. Lithium salts are preferred because their cations are easily coordinated and solvated to exhibit their ionic conductivity character. However, the interest in polymer electrolytes containing trivalent lanthanide ions has grown considerably. Lanthanide metal ions were incorporated as triflate salts like erbium triflate ($\text{Er}(\text{CF}_3\text{SO}_3)_3$) into membranes to produce innovative and very attractive NIR-emitting polymer electrolytes. Incorporating salt in polymers leads to various changes in their structure and optical and thermal properties and, over the last years, lanthanides have been used because of their luminescent properties [19,20]. Materials doped with erbium have a lot of interest in view of applications in optoelectronics. Specially, these materials, in trivalent state (Er^{3+}), are very attractive for lasers and optical amplifiers due to the transition from their first excited state ($^4\text{I}_{13/2}$) to the ground state ($^4\text{I}_{15/2}$), which occurs at a wavelength of 1.54 μm , one of the standard telecommunication wavelengths [21].

In the present study, samples behaviour was evaluated by thermal

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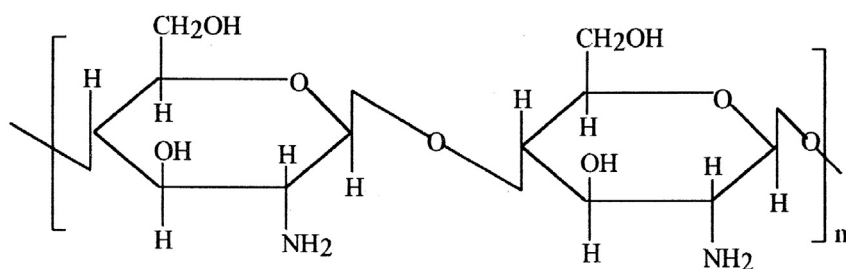


Fig. 1. Chemical structure of chitosan [14].

Table 1
Relevant data of the preparation of chitosan-erbium based electrolytes.

Samples designation	n (g)	m (g)
CS(ErTrif) _{0.05} Gly _{0.25}	0.05230	0.25276
CS(ErTrif) _{0.10} Gly _{0.25}	0.10204	0.25748
CS(ErTrif) _{0.15} Gly _{0.25}	0.15456	0.25471
CS(ErTrif) _{0.20} Gly _{0.25}	0.20250	0.25963
CS(ErTrif) _{0.25} Gly _{0.25}	0.25312	0.25702
CS(ErTrif) _{0.05} Gly _{0.70}	0.05511	0.70680

analyses such as thermogravimetric (TGA) and differential scanning calorimetry (DSC), impedance spectroscopy measurements, X-Ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and atomic force microscopy (AFM). The electrolyte prepared with erbium triflate salt and higher glycerol amount was applied in a small smart window with glass/ITO/PB/electrolyte/CeO₂-TiO₂/ITO/glass configuration, which electrochemical and spectral characteristics were recorded.

2. Experimental

2.1. Samples preparation

The electrolytes were prepared by the solvent-casting method and according to the method reported previously [22]. The host polymer chitosan (0.20 g, Sigma-Aldrich; medium molecular weight) was dissolved in 10 mL of 1% acetic acid solution (Sigma-Aldrich) and under magnetic stirring overnight for complete dissolution. The next day,

different quantities of erbium (III) trifluoromethanesulfonate (erbium triflate; Sigma-Aldrich, 98%) as salt and 0.25 g of glycerol (Himedia, 99.5%), acting as plasticizer, were added to this solution under stirring. One more sample was synthesized using the same mass of polymer (0.20 g), 0.05 g of salt, and a greater glycerol quantity (0.70 g). This sample was used for comparison with the sample with the same salt amount but a lower glycerol quantity. Samples have been represented by the notation CS(ErTrif) _{n} Gly _{m} , where n and m are the mass of the erbium triflate salt and glycerol in the electrolytes, respectively, according to the Table 1. When the solutions were homogeneous, they were poured on plastic Petri plates and left to dry at room temperature until film formation. Then, the films were subjected to a final drying for about two days in an oven, which temperature was raised from 30 to 60 °C and periodically evacuated and purged with dry argon. After this process, the samples were conditioned in a glovebox under argon atmosphere. Fig. 2 has a physical appearance picture of one of these samples. The thickness of the samples was determined using a micrometer (Mitutoyo) and it varied between 0.132 and 0.270 ± 0.001 mm.

2.2. Characterization techniques

Electrolyte sample sections were subjected to thermal analysis. The thermogravimetric analyses (TGA) were made using a TGA instrument TGA-Q500, London, in 25–900 °C temperature range. For differential scanning calorimetry (DSC) measurements the samples were placed in 40 µL aluminium cans with perforated lids to permit the release and removal of decomposition products. The electrolytes were analysed under a flowing argon atmosphere using a Mettler DSC 821e, Switzerland, in a temperature range between –25 to 200 °C and at a heating rate of 5 °C min⁻¹.

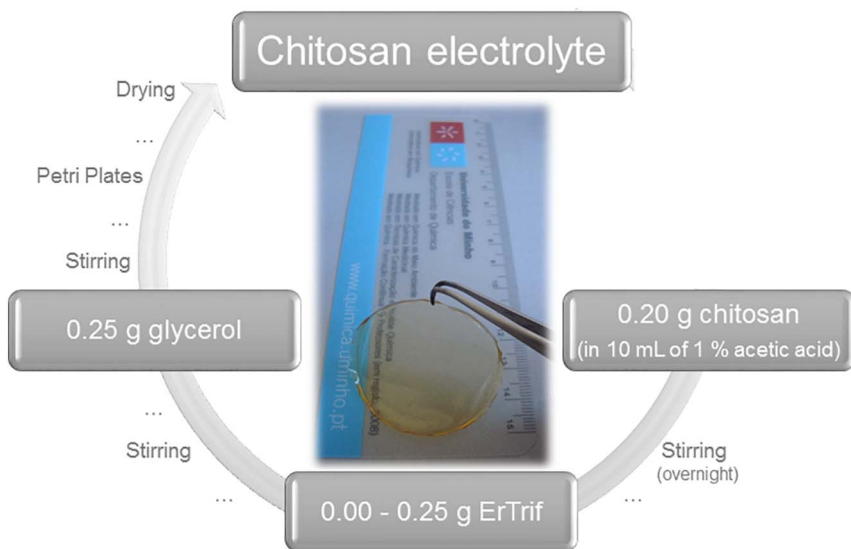


Fig. 2. Preparation scheme and physical appearance of the samples.

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