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Innovative electrolytes based on chitosan and thulium for solid state applications: Synthesis, structural, and thermal characterization

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ABSTRACT

Innovative chitosan-based polymer electrolytes, plasticized with glycerol and doped with thulium triflate ($Tm(CF_3SO_3)_3$) were prepared by solvent casting technique and their properties were evaluated. The samples are thermally stable up to about 130 °C and the degradation process occurs in three stages in the case of samples containing salt. The DSC curves have shown that the addition of salt produces no significant changes in the thermograms, and the SEM micrographs indicated that the addition of salt does not promote changes of the sample surface. AFM analysis revealed that the samples' roughness increases when higher glycerol amount is added. The sample doped with 20.56% of thulium triflate exhibits ionic conductivity of 10^{-7} S cm^{-1} at 30 °C and 10^{-6}–10^{-5} S cm^{-1} at 90 °C. For the same sample but with high glycerol amount the ionic conductivity increases to 10^{-5} S cm^{-1} at 30 °C and 10^{-4} S cm^{-1} at 90 °C. Due to the highest conductivity values, this sample was chosen to assemble electrochromic device (ECD) and the obtained results confirm that it is promising material to be applied in ECDs.

1. Introduction

In recent years, researches have been studied natural polymers, like polysaccharides, as hosts for polymer electrolytes application. Natural polymers have attracted attention because they are abundantly available in nature, have a low cost, are biocompatible and biodegradable, inert, safe, and non-toxic [1]. However, solid polymer electrolytes (SPEs) based on natural polymers present some differences when compared with synthetic ones. Among them, there can be cited a low thermal stability and relatively low conductivity, but even though both seem to be sufficient for the proposed applications such as electrochemical devices [2,3]. Additionally, plasticization process is a way to overcome this problem [4]. Addition of plasticizers also promotes a possibility of producing transparent membranes with good adhesion properties to glass and metal surfaces [5]. It is because the plasticizers reduce the local viscosity of the polymer matrix, facilitating the ions mobility, which results in the ionic conductivity enhancement [6].

There are many natural polymers used as host in SPEs, and chitosan is an interesting example. It is a biopolymer obtained from chitin, the second macromolecule most produced after the cellulose. Chitosan is an explored polymer due to its biodegradability, biocompatibility, non-toxicity, and absorption properties, and it is studied as polymer matrix for ionic conduction [7,8]. Its structure contains several polar groups (OH and NH_2) as can be seen in Fig. 1, and these polar groups can act as electron donors and interact with inorganic salts [9]. Some studies revealed that the cation of a salt can coordinate at nitrogen and/or oxygen atoms in chitosan [10,11]. As an example, FTIR analysis of chitosan and NH_4NO_3 electrolytes have shown the complexation between the cation of the salt and the nitrogen of the amine functional group [12,13]. On another hand, doping polymer matrices with salts can increase the amorphous content and contributes to enhancement of the conductivity of the electrolytes [14].

In present work, plasticized electrolytes based on chitosan and thulium triflate were prepared. Chitosan was dissolved in diluted acetic acid solution, glycerol was used as plasticizer, and the solution was cast to form a film. The use of trivalent rare earth cations is stimulated by the possibility to obtain materials with luminescent behaviour thereby creating new opportunities for innovative devices [16]. Thulium is used in electroluminescent devices, and it is a blue emitter from its $^3P_0$, $^1D_2$, and $^1G_4$ levels [17]. Tm^{3+} exhibits light emission at about 480 nm [18]. In a study of organic electroluminescent devices, using thulium complexes, a third step of the mechanism of blue light emission from Tm^{3+} is a transition $^1G_4 \rightarrow {}^3H_6$, which gives rise at 482 nm [19]. In the case of the present study, the electrolytes prepared with thulium triflate salt were applied in smart windows and their performances were evaluated. Samples behaviour was evaluated by impedance spectroscopy measurements,

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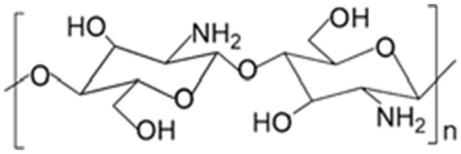


Fig. 1. Structure of chitosan [15].

thermal analysis (thermogravimetric analysis - TGA and differential scanning calorimetry - DSC), scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-Ray diffraction (XRD). Luminescent measurements were also performed, but no signal was observed. Finally, these ionically conducting membranes were applied in small electrochromic devices with glass/ITO/PB or WO_3/electrolyte/CeO_2-TiO_2/ITO/glass configuration, and their electrochemical and spectral characteristics were recorded.

2. Experimental section

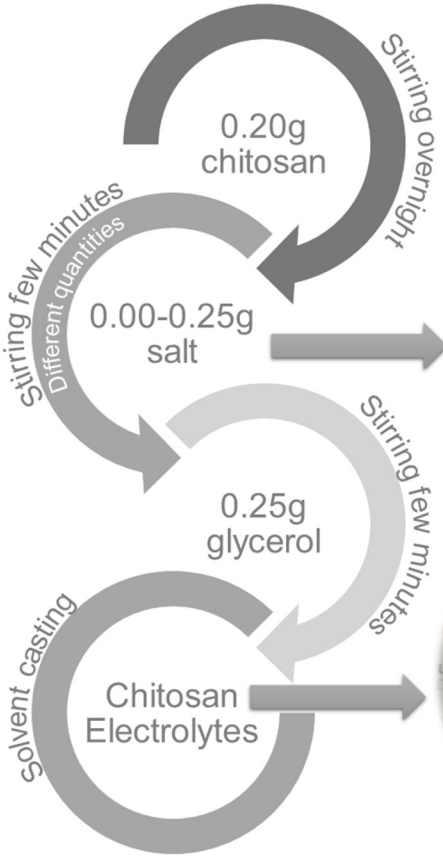
2.1. Samples preparation

Samples were prepared by dispersion of 0.20 g of chitosan (Sigma-Aldrich; medium molecular weight) in 10 mL of 1% acetic acid solution (Sigma-Aldrich) under magnetic stirring overnight for complete dissolution as reported elsewhere [20]. Thulium (III) trifluoromethanesulfonate was prepared by addition of trifluoromethanesulfonic acid (Merck, 98%) to an excess of thulium oxide (Aldrich, 99.9%), and this aqueous suspension was stirred until pH approached neutrality as described by Silva et al. [21]. Thulium triflate as salt, in different quantities, and 0.25 g of glycerol (Himedia; 99.5%) were added to this solution, which was stirred for few minutes. Acetic acid solution was used to dissolve chitosan, and glycerol was added to promote plasticization of the samples. Samples have been represented by the notation $Chit_nTm(Trif)_3$, where n is the percentage of the thulium triflate salt proportion in the electrolytes (Fig. 2). Based on a previous study on the effect of glycerol on the conductivity values of the samples containing chitosan and cerium triflate [22], a new sample was prepared using 0.20 g of chitosan, 0.05 g of thulium triflate and 0.70 g of glycerol. Thulium amount was chosen based on the maximum conductivity value obtained for this system. The samples were represented by the notation $ChitTmTrif_xGly_y$, where $x = 0.05$ g is the thulium mass used, and y is the glycerol amount ($y = 0.25$ or 0.70 g).

The resulting solutions were then poured on Petri plates, cooled at room temperature, and then dried in an oven between 25 and 60 °C for two days to form transparent membranes (Fig. 2). The thickness, which varied between 0.063 and 0.239 ± 0.001 mm was determined with a micrometer (Mitutoyo). After drying process, samples were stored in glovebox under argon atmosphere.

2.2. Measurement techniques

The total ionic conductivity was determined by introducing an electrolyte disk between two 10 mm diameter ion-blocking gold electrodes (Goodfellow, >99.95%) to form a symmetrical cell. The electrode/chitosan electrolyte/electrode assembly was placed in a suitable constant-volume-support and installed in a Büchi TO51 tube-oven. The K-type



Sample	$Tm(CF_3SO_3)_3$ Mass ± 0.00001 (g)	Thickness ±0.001 (mm)
$Chit_{0.00\%}Tm(Trif)_3$	0.00000	0.145
$Chit_{5.47\%}Tm(Trif)_3$	0.01198	0.146
$Chit_{20.56\%}Tm(Trif)_3$	0.05263	0.063
$Chit_{33.89\%}Tm(Trif)_3$	0.10340	0.096
$Chit_{42.57\%}Tm(Trif)_3$	0.15090	0.083
$Chit_{49.69\%}Tm(Trif)_3$	0.20140	0.192

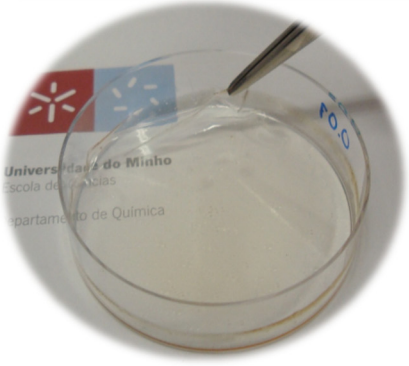


Fig. 2. Samples preparation scheme, used salt mass, thickness, and physical appearance of chitosan-thulium-based electrolytes.