Gellan gum—Ionic liquid membranes for electrochromic device application

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ABSTRACT

Biopolymer-based materials have been of particular interest and they are alternatives to synthetic polymers based on the decreasing oil resources. The polymer electrolytes were doped with choline-based IL N,N,N-trimethyl-N-(2-hydroxyethyl)ammonium bis(trifluoromethylsulfonyl)imide ($[N_{1\ 1\ 2(OH)}][NTf_2]$), or Er $(CF_3SO_3)3$ or both. The polymer electrolytes were employed in the production of glass/ITO/WO_3/electrolyte/CeO_2–TiO_2/ITO/glass electrochromic devices (ECDs). The lowest onset temperature for the degradation of all the SPEs is at ~130 °C for the Gellan Er $(CF_3SO_3)_3$ (10:1) this temperature range of stability is wide enough for a material to be applied as an electrolyte/separator component in electrochemical devices.

The three ECDs displayed fast switching speed (ca. 15 s). Gellan $[N_{1\ 1\ 2(OH)}][NTf_2]$ Er $(CF_3SO_3)_3$ (5:1:10) exhibited an electrochromic contrast of 4.2% in the visible region, the coloration efficiency attained at 555 nm was 3.5 and 0.90 $cm^{-2}\,C^{-1}$ in the "colored" and "bleached" states, respectively, and the open circuit memory was 48 h. Preliminary tests performed with a prototype electrochromic device (ECD) incorporating WO_3 as cathodic electrochromic layer, are extremely encouraging.

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1. Introduction

Solid polymer electrolytes (SPEs) have been proposed as substitutes for conventional non-aqueous electrolytes in various electrochemical devices. These promising materials may be of interest in various practical devices including batteries, sensors and electrochromic displays [1,2]. The main advantage when compared with liquid electrolytes is that they can offer high performance in terms of specific energy and specific power (batteries), safe operation, flexibility in device architecture and low manufacturing costs [3].

Ionic liquids receive a lot of attention during the last decade [4]. A large number of publications have appeared describing their electrochemistry, thermal stability, good conductivity and almost null volatility [4]. Other aspects such as wide electrochemical window, recyclability and non-flammability are also discussed [5]. Consequently their promising physical and chemical properties turned them as interesting materials for electrochemical synthetic processes [6] and in the evaluation of the redox behavior of electroactive substrates [7,8]. They started also to be investigated for electrochemical technologies, such as batteries, fuel and solar cells, photovoltaic devices and metal deposition [9].

Gellan gum is an anionic polysaccharide produced by the fermentation of pure culture of *Sphingomonas elodea* [10,11]. This heteropolysaccharide is basically composed of repetitive units of tetrasaccharides consisting of two glucoses (Glc), one glucuronic acid (GlcA) and one rhamnose (Rha) rings [12,13]. The main advantage of this natural macromolecule when compared with other ones is its high thermal stability and thermo-reversibility, i.e. showing the reversible properties under heating and cooling [14].

Recently, natural macromolecule-based ionically conducting membranes containing ionic liquids (ILs) have been prepared and characterized [15,16]. Moreover, these samples were also applied in small electrochromic devices revealing electrochemical reversibility of 200 color/bleaching cycles [15–17].

Aiming to progress on natural macromolecules and ionic liquid studies for electrochemical device applications the present work presents the results of the characterization of polymer electrolytes using gellan gum as matrix. Different samples were obtained by adding erbium triflate and/or the ionic liquid, N,N,N-trimethyl-N-(2-hydroxyethyl)ammonium bis(trifluoromethylsulfonyl)imide, $[N_{1\ 1\ 2(OH)}][NTf_2]$.

Solvent-free electrolyte membranes were prepared and characterized by ionic conductivity measurements, thermal analysis, cyclic voltammetry, X-ray diffraction (XRD) scanning electron microscopy (SEM) and atomic force microscopy (AFM).

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2. Experimental section

2.1. Materials

The IL used, $[N_{1\,1\,2(OH)}][NTf_2]$ was synthetized with a purity higher than 99% as described in a previous paper [18]. In order to reduce water and volatile compounds to negligible values, the IL was dried under low pressure of 10^{-1} Pa and vigorously stirred at a moderate temperature of ca. 47 °C for at least a day. Coulometric Karl–Fischer titrations (Metrohm 831 KF Coulometer) revealed levels of water, always below 300 ppm. This value is a conservative estimate that takes into account the uncertainty associated with the handling of the IL.

$Er(CF_3SO_3)_3$ was synthetized according to the method described elsewhere [19].

2.2. SPE preparation

The electrolytes were prepared by the solvent-casting method. The host polymer gellan gum (0.5 g, Sigma-Aldrich) was dissolved in 50 mL of Milli-Q water, heated under magnetic stirring for a few minutes up to room temperature for a complete dissolution. A mass of 0.25 to 0.10 g of $[N_{1\,1\,1\,2(OH)}][NTf_2]$ and 0.5 g of glycerol (Himedia, 99.5%), acting as plasticizer, were added to this solution under stirring. After that, the solution was casted on Petri dishes and let to dry up at room temperature to form a transparent membrane. The film was finally transferred to an oven at 60 °C, aged for 8 to 12 days, dried in a vacuum and stored in an argon atmosphere to avoid moisture adsorption. Based on the terminology adopted previously [20], the notations Gellan $[N_{1\,1\,1\,2(OH)}][NTf_2]$ (2:1), Gellan $[N_{1\,1\,1\,2(OH)}][NTf_2]$ (2.5:1) and Gellan $[N_{1\,1\,1\,2(OH)}][NTf_2]$ (5:1) express the content of IL 0.25, 0.20 and 0.10 g, respectively.

Other polymer electrolytes containing $Er (CF_3SO_3)_3$ were prepared using the same methodology. The notations Gellan $Er (CF_3SO_3)_3$ (5:1), Gellan $Er (CF_3SO_3)_3$ (10:1) and Gellan $Er (CF_3SO_3)_3$ (12.5:1) express the content of 0.10, 0.05 and 0.04 g of erbium salt, respectively. Finally, polymer electrolyte incorporating both the IL and erbium salt was prepared and named Gellan $[N_{1\,1\,1\,2(OH)}][NTf_2]$ $Er (CF_3SO_3)_3$ (5:1:10).

2.3. Characterization techniques

For bulk conductivity measurements, an electrolyte sample disk was placed between two 10 mm diameter ion blocking gold electrodes (Goodfellow, >99.9%). The electrode/electrolyte sample/electrode assembly was secured in a suitable constant-volume support, which was installed in a Buchi TO 51 tube oven. A calibrated type K thermocouple, placed close to the electrolyte disk, was used to measure the sample temperature with a precision of about ± 0.2 °C and samples were characterized over a temperature range of between 25 and 100 °C. Bulk conductivities of the samples were obtained during heating cycles using the complex plane impedance technique (Autolab PGSTAT-12 (Eco Chemie)) over a frequency range of 65 kHz to 0.5 Hz.

The cell was secured in a suitable constant volume support. The ionic conductivity (σ) was determined using the expression:

$$\sigma = \frac{t}{A * R_b} \tag{1}$$

where t is the thickness, A is the area and R_b is sample bulk resistivity, obtained by interception of the imaginary impedance (minimum value of Z″) with the slanted line in the real impedance (Z′).

The evaluation of the electrochemical stability window of electrolyte compositions was carried out under an argon atmosphere, at room temperature and within a Faraday cage, using a two-electrode cell configuration: a 25 μm diameter gold microelectrode as the working electrode and a lithium disk (cut from Aldrich, 99.9%; 19 mm diameter, 0.75 mm thick) as counter and reference electrodes. An Autolab PGSTAT-12 (Eco

Chemie) equipment was used to record voltammograms at scan rates of 1.0, 0.5, 0.1 and 0.05 V s^{-1}.

The thermal behaviour of the membranes was evaluated by differential scanning calorimetry (DSC) between -60 and 200 °C, at a heating rate of 5 °C min^{-1}, under a flowing argon atmosphere, using a Mettler DSC 821e differential scanning calorimeter. Samples were transferred to 40 μL aluminium cans with perforated lids within a dry argon-filled glove box.

Scanning electron microscopy (SEM) micrographs were obtained using a SEM/ESEM-FEI Quanta 400 scanning electron microscope at high acceleration voltage (20 kV). A small portion of each sample was cut, fixed on an aluminium stub with carbon tape and then coated with Au/Pd.

XRD patterns were recorded at room temperature with a PANalytical X'Pert Pro diffractometer equipped with a X'Celerator PW3015/20 detector using monochromated CuK$_a$ radiation (λ = 1.54 Å) between 2θ = 10 and 60° with a resolution of 0.02°. The samples were not submitted to any thermal pre-treatment.

AFM topographic images were obtained in a Nanosurf EasyScan 2 AFM, working in the non-contact mode and equipped with a silicon (Si) probe with a resonance frequency of 190 kHz and a force constant of 48 N m^{-1}. The surface roughness was calculated as root mean square (RMS) height or RMS surface roughness (Sq).

Electrochromic devices with glass/ITO/WO$_3$/electrolyte/CeO$_2$-TiO$_2$/ITO/glass configurations were obtained by assembling the 2 pieces of coated glasses. Electrolytes in the form of hydrated membranes were deposited on glass/ITO/WO$_3$ coatings and 1 cm free space was left for the electrical contact. Then the other coated substrate glass/ITO/CeO$_2$–TiO$_2$ was pressed onto the membrane in such a way that the two coatings faced each other inside the assembled window. A 1 cm wide Cu-conducting tape (3 M) was glued to the free edge of each substrate for electrical connection. The mounted cells were finally sealed with a protective tape (3 M).

The electrochemical measurement characterization of the ECDs was performed with an Autolab 302 N equipment. For the cyclic voltammetry measurements a tension ranging from -2.0 to $+1.8$ V was applied with an electric field scan step of 50 mV s^{-1}. For the chronoamperometric measurements a square wave at -2.0 V for 15 s and $+1.8$ V for 15 s was applied.

3. Results and discussion

3.1. Electrochemical studies

The electrochemical window is an important parameter to be evaluated when applications in electrochemical devices is intended. The electrochemical stability window of the gellan gum-based membranes doped with different ILs was determined by CV, at room temperature over the -2.0 to 6.0 V potential at four different scan rates: 1.0, 0.5, 0.1 and 0.05 V s^{-1} (Fig. 1). In the CV plot the sweep potential was firstly scanned in the positive direction and then in the reversed direction (Fig. 1). Fig. 1 reveals the good electrochemical stability of the Gellan $[N_{1\,1\,1\,2(OH)}][NTf_2]$ $Er (CF_3SO_3)_3$ (5:1:10) membrane. These voltammograms demonstrate that in the anodic region the sample is stable up to about 3.0 V versus Li/Li$^+$, whereas in the cathodic region it is stable up to about -0.5 V versus Li/Li$^+$. This means that the overall redox stability of the membrane spans about 3.5 V, an acceptable stability window for an application in a solid-state electrochemical device.

The ionic conductivities of the Gellam gum-based polymer electrolytes are modest. In these systems the ionic transport is promoted by the hopping of ionic species. The ionic conductivity depends strongly on two factors, such as, salt concentration and temperature.

The values of the conductivity at 30 °C and 90 °C, for all prepared samples are listed in Table 1.

The highest room temperature (T = 30 °C) conductivity (5.21 $\times$ 10^{-6} S cm^{-1}) was registered for the Gellan $[N_{1\,1\,1\,2(OH)}][NTf_2]$ (5:1)