Optik 135 (2017) 85–97

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Original research article

Preparation and characterization of protonic solid electrolyte applied to a smart window device with high optical modulation

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A R T I C L E I N F O

Article history:
Received 9 November 2016
Received in revised form 22 January 2017
Accepted 23 January 2017

Keywords:
Gelatin
Solid electrolyte
Smart window
Ionic conducting membranes

A B S T R A C T

Solid electrolytes based on gelatin, cross-linked with formaldehyde and containing different quantities of glycerol, acetic acid and/or hydrochloric acid, with preparation routine modification have been conducted and characterized using X-ray diffraction, mechanical test, impedance spectroscopy and UV–vis spectrophotometry.

The x-ray investigation revealed that all the prepared layers are predominantly amorphous and are influenced noticeably by the addition of different quantities of plasticizer as well acids. The tensile, elongation at break and modulus of the prepared membranes are evaluated and discussed. Using impedance spectroscopy, it was found that, the ionic conductivity acquired a maximum value of 1.28×10^{-5} S/cm at 26 wt% acetic acid contents, then decreases at higher concentration due to ion pair formation. The optical investigation revealed transmission $\geq$98% at wavelengths >580 nm. Optimized membrane that has both high conductivity, high transparency, mechanical stability and show good adhesion to both counter and working electrodes was successfully applied to an electrochromic smart window device including tungsten and nickel oxides as electrochromic layers. Using cyclic voltammetry (CV), chronoamperometry (CA), and the device performance has been characterized at different working voltages. The device showed reversible blue coloration, high lifetime cyclic stability, and long-term open circuit memory. The coloration efficiency η_{600} is enhanced reaching a value 38.1 cm^2/C. Such results indicate that protonic gelatin-based solid electrolyte is a good candidate as ionic conductor layer in EC devices and of technological and commercial interest.

1. Introduction

Development and applications of electrochromic devices (ECDs) have gained great interest, principally due to the growing use of automotive electrochromic (EC) rear view mirrors [1] which enable glare attenuation during night, and EC smart

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http://dx.doi.org/10.1016/j.ijleo.2017.01.056

windows with its possibility of saving the energy by controlling flow of light and heat transmitted through the glazing of buildings, vehicles, trains, aircrafts, etc. [2]. This interesting phenomena lead to many other applications, such as sunroofs, shades, visor, skylight, displays, light filter and screens for light pipe displays and other electro-optical devices [3,4]. The common configuration of the smart window device is (transparent conductor (TC)/cathodic EC thin film/solid electrolyte/anodic EC thin film/TC) [5,6]. WO_3 and NiO thin films are the most commonly used materials as cathodic and anodic EC thin films respectively [7–9]. The favorable characteristics of these two metal oxides include reversible transmittance high modulation when the electric field is established, reversibility to cycle operation and high stability during operation make them the most used EC components in EC devices.

ECDs with solid state EC working and counter Electrodes thin coatings have been built with various electrolytes, containing mobile proton or lithium charge species [4]. In such devices, solid polymeric electrolytes (SPEs), whose functioning plays an important role in the device performance, have emerged as important ionic conducting materials, as they offer some advantages over liquid electrolytes, such as operation at higher temperatures, no flowing and corrosion after damage, and ease of application to electrochemical devices. In addition, SPEs received much interest due to their good adhesion to the electrodes, very limited problems with leakage or pressure-related distortions, their simple preparation in different forms and good mechanical properties [10,11].

Recently, attention has been focused on low cost, abundant and renewable sources for solid electrolytes, namely, natural polymers to replace the existing traditional synthetic polymeric electrolytes. As examples, modified starch [12,13], Chitosan [14–16], or gelatin [17–19] grafted hydroxyethylcellulose [20], hydroxypropyl-cellulose [21], have been used to prepare electrolytes releasing H^+ or Li^+ ions with ionic conductivity values in the order of 10^{-5} S/cm at room temperature. Very recently the fabrication of small ECDs using SPEs from natural polymers with good coloring/bleaching properties have been reported [12,22–25].

Natural gelatin is considered as a new polymeric matrix comprising a component of ECD [26]. Recent studies on gelatin-based electrolytes containing, glycerol as plasticizer and $LiBF_4$ as salt have been conducted [27]. Results obtained from proton nuclear magnetic resonance, continuous-wave and pulsed electron paramagnetic resonance of gelatin-based polymer gel electrolytes containing acetic acid [28] or hydrochloric acid [29], have been discussed. A solid-state ECD incorporating electrolytes based on gelatin doped lithium perchlorate and acetic acid have been fabricated [30]. Gelatin based acetic acid as protonic conductor and applied for an ECD [31].

Most recently, amorphous ion conducting membranes of gelatin plasticized by glycerol and contained Li/I_2 have been prepared and characterized. ECD fabricated with these SPE produced 20% optical modulation [32]. Polymer electrolytes based on gelatin matrix doped with europium triflate have been prepared and the samples were applied to a small ECD, which showed insertion/extraction process during chronoamperometric cycles [33]. Gelatin-based electrolytes doped with a range of concentrations of zinc triflate ($Zn(CF_3SO_3)_2$) have been synthesized and applied to an ECD with (glass/ITO/WO_3/gelatin-based electrolyte/CeO_2-TiO_2/ITO/glass) configuration [34]. Very recently, gelatin-HCl protonic gel polymeric electrolytes were studied and the results showed that the influence of glycerol is more pronounced than the influence of acid on ionic conductivity values [24]. The reported studies, showed that gelatin-based solid electrolyte (GSE) well-suited as multi-functional component (ionic conductor, separator, adhesive and sealant) in ECDs, owing to their physical properties [22].

2. Objectives

As seen from literature, there is a remarkabl interest in the developing of solid polymer electrolytes based on the natural polymeric matrix, as potential ionic conductors in ECDs.

In a previous paper, GSEs doped with LiCl have been prepared, characterized and successfully applied to a small EC smart window device [35]. Following these research tendencies, the present work deals with the development of transparent gelatin-based proteins solid electrolytes (GPSEs), synthesized from water-soluble gelatin, and possessing high conductivity, as possible candidates for application in EC smart window devices. The developed membranes doped with different quantities of glycerol, hydrochloric acid or acetic acid. The developed GPSEs are applied as an ionic conductor component in a complimentary ECD with the configuration, (glass/FTO/WO_3/GPSE/NiO/FTO/glass).

3. Experimental

3.1. Preparation of protonic solid electrolyte

Three groups of GPSEs have been prepared with different quantities of different dopants according to the following;

1. Samples S_{11}, S_{12}, S_{13}, S_{14}, S_{15} have been prepared with different glycerol contents as given in Table 1. Two grams of commercial uncolored gelatin (Kraft food company, Portugal) were dispersed in 15 ml of boiled distilled water, then placed on the magnetic stirrer for a few minutes until the temperature lowered to 50 °C for complete dissolution. A quantity of 0.25 g of formaldehyde as cross-linking, and 0.95 ml acetic acid were added to prevent fast solidification of the electrolyte then different quantities of glycerol as a plasticizer in the range 13–32 wt% were dispersed in solution under stirring. The viscous solution is then cooled down to 30 °C and poured in Petri plates to form transparent films, then kept in a desiccator. The modification to the preparation routine by dispersion of the powder in hot solution then cooling