

Gelatin in electrochromic devices

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ABSTRACT

A gelatin-based electrolyte has been developed and characterized by impedance spectroscopy and thermal analysis. These electrolytes are promising materials to be applied in electrochromic devices because gelatine is a material available in nature, it is cheap, easy to handle and to prepare.

In this study the characterization of a solid-state electrochromic device based on gelatin is reported and results obtained suggest that this electrolyte is very attractive for electrochemical device applications. Gelatin-based electrolytes were successfully used in the assembly of prototype electrochromic devices (ECDs) and exhibited good optical density. The ECD display incorporating gelatine I and gelatine II samples presented in the visible region an average transmittance above 68% in the bleached state. After coloration the structure assembled with gelatine I composition presented an average transmittance in the visible wavelength region above 21% and 36% for gelatin II.

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1. Introduction

Recent reports indicate alternative energy sources as one of the global challenges that need to be addressed on an urgent basis. Electrochromic materials have been attracting much interest for several decades and received a great deal of attention due to their important applications, such as electrochromic windows, rear-view mirrors, electrochromic displays and electronic paper or electrochromic painting [1].

Electrochromic windows can be effectively used in a building to check heating and cooling loads and can make a significant difference in the energy consumption. In fact, these energy efficient windows used in either new or retrofit situations can cut annual energy costs by up to 15%, if employed properly. Electrolytes, which are ubiquitous in all solid-state devices, are of profound interest to electrochemists, who transform these materials into interesting multi-functional systems with great potential in many applications [2,3].

There is an increased interest in developing solid polymer electrolytes (SPEs) by using different polymeric matrix to produce new technological products. A first work was published by Oliveira et al. [4] who presented some studies carried out using commercial gelatin to produce a new polymeric matrix as a component of an electrochromic device. The electrolyte produced was based on bismuth and copper salts. Recent attention has been focused on the use of natural polymers due to their biodegradability, low production cost

and good physical and chemical properties. These polymers are usually used in the cosmetic, pharmaceutical and food industries, but can also be used as polymeric networks in SPEs.

In this work the results of the preliminary studies of solid-state electrochromic devices incorporating materials based on gelatin doped with lithium perchlorate are reported. A gelatin-based electrolyte has already proved to be well-suited as multi-functional component (electrolyte, separator, adhesive and sealant) in electrochromic devices, owing to their good mechanical, chemical, thermal and electrochemical properties [5].

2. Experimental

2.1. Materials

2.1.1. Counter-electrode

The $(\text{CeO}_2)/\text{TiO}_2$ was prepared by dissolving $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Cerium (III) nitrate hexahydrate, Fluka, $\geq 98\%$ purity) and $\text{Ti}(\text{OPr})_4$ Titanium (IV) isopropoxide (Fluka, purum), in anhydrous ethanol by stirring the sol at 30 °C during several days (typically 120 h) under argon atmosphere. Such sols are stable several months when kept in a refrigerator at -18 °C.

2.1.2. Transparent conductive oxide (TCO)

Transparent conductive oxide: Indium doped zinc oxide films (IZO) were deposited on glass substrates by rf (13.56 MHz) magnetron sputtering using a ceramic oxide target $\text{In}_2\text{O}_3 \cdot \text{ZnO}$ (92:8 wt%; 5 cm diameter, Super Conductor Materials, Suffern, NY, USA) with a

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purity of 99.99%. Sputtering was carried out at room temperature, with an argon flow of 20 sccm and an oxygen flow of 0.4 sccm keeping the deposition pressure (argon and oxygen) constant to a value of 0.15 Pa. The distance between the substrate and the target was 10 cm and the rf power was held constant at 100 W.

2.2. Gelatin-based electrolyte

2.2.1. Gelatin-based electrolyte I

In a glass flask, 2 g of commercial animal gelatin supplied by Jerónimos was added to 15 mL of ultra-pure water at 50 °C under stirring until it dissolves completely. After this, 0.5 mL of glycerol supplied by Roth was added to the previous solution and stirred for 10 min, 0.25 mL of formaldehyde 37% (Merck) was added to this solution. In another glass flask, 0.3 g of lithium perchlorate (Fluka) and 0.5 g of peptone from casein (Merck) were added to 1 mL of ultra-pure water and 0.5 mL of acetic acid 0.1 M under stirring. After complete dissolution, the second mixture was added to the first one and stirred for 10 min. Thin films of the final solution were made on parafilm with a glass ring. Twenty-four hours later the film was detached from the parafilm and was encapsulated by two substrates: one with a TCO and a counter-electrode (Ce-Ti) deposition and the other with a TCO and an electrochromic material (WO_3) deposition.

2.2.2. Gelatin-based electrolyte II

The same as gelatin I-based electrolyte except for the amount of lithium perchlorate, which in this case it was used 0.6 g.

2.3. Electrochromic material

Tungsten oxide films with 300 nm were deposited on transparent conductive oxide coated glass substrates by rf magnetron sputtering using a WO_3 ceramic oxide target from Super Conductor Materials with a purity of 99.99%. Sputtering was carried out at room temperature, under an argon and oxygen atmosphere keeping the deposition pressure constant to a value of 2.6 Pa. The distance between the substrate and the target was 10 cm and the rf power was held constant at 200 W.

2.4. Electrochromic cell assembly

Device assembly was carried out direct application of a small volume of the gelatin-based electrolytes to the surface of a glass plate onto which a IZO/ WO_3 coating had been previously deposited. The gel was dried in a vacuum oven for a period of 7 days. The thicknesses used for the electrolyte, IZO and WO_3 component layers were 100, 170 and 400 nm, respectively. A second IZO coated glass plate was placed on top of the dry electrolyte layer and the two plates were pressed together to spread the electrolyte in a thin film between the electrochromic surfaces. The entire assembly (the size of $3.5 \times 2.5 \text{ cm}^2$ were obtained by assembling) procedure described was carried out under a laboratory atmosphere.

2.5. Measurements

2.5.1. Thermal analysis

Electrolyte sample sections were subjected to thermal analysis under a flowing argon atmosphere between 25 and 250 °C and at a heating rate of 5 °C min^{-1} using a Mettler DSC 821e. All samples were presented for analysis in 40 μL aluminium cans with perforated lids to permit the release and removal of decomposition products.

Samples for thermogravimetric studies were prepared in an identical manner, transferred to open platinum crucibles and ana-

lyzed using a Rheometric Scientific TG 1000 thermobalance operating under a flowing argon atmosphere. A heating rate of 10 °C min^{-1} was used to analyze all the samples.

2.5.2. Impedance spectroscopy

Total ionic conductivities of electrolyte samples were determined using a constant volume support equipped with gold blocking electrodes and located within a Buchi TO 50 oven. The sample temperature was evaluated by means of a type K thermocouple placed close to the electrolyte film and impedance measurements were carried out at frequencies between 65 kHz and 500 MHz with a Solartron 1250 FRA and 1286 ECI, over a temperature range from 20 to 90 °C. Measurements of conductivity were effected during heating cycles. The reproducibility of recorded conductivities was confirmed by comparing the results obtained for a sample subjected to two heating–cooling–heating cycles. This procedure demonstrated the correct operation of the support and the mechanical stability of the samples.

2.5.3. Optical properties

The optical transmittance measurements were performed with a Shimadzu UV/vis 3100PC double beam spectrophotometer in the wavelength range from 380 to 800 nm. The films thickness were measured using a surface profilometer (Dektak 3D from Solan Tech).

3. Results and discussion

3.1. Thermal behaviour of electrolytes

Fig. 1 shows the changes in mass for different samples upon heating. In this study it was investigated the process of liberation of the water from the system water–gelatin and evaluated the weight losses during heating. Before drying the electrolyte, for pure gelatin, the water content decreases continuously up to 120 °C. The pure gelatin also show the second decrease in mass, which is attributed to the thermal degradation. This change has already been cited by A. Pawlicka et al. [6] as endothermic hydrolysis and oxidation process followed by exothermic reaction, which start at 340 °C and corresponds to final pyrolysis. For the other samples (gelatin I, gelatin II), an abrupt decrease in mass up to 100 °C is observed, due to the great amount of water that leaves the system. After this temperature, the decrease in weight was not so abrupt, but it shows that a certain amount of water still remains in these samples and is being slowly released. In a second phase of the study, the electrolyte samples were dried at 120 °C

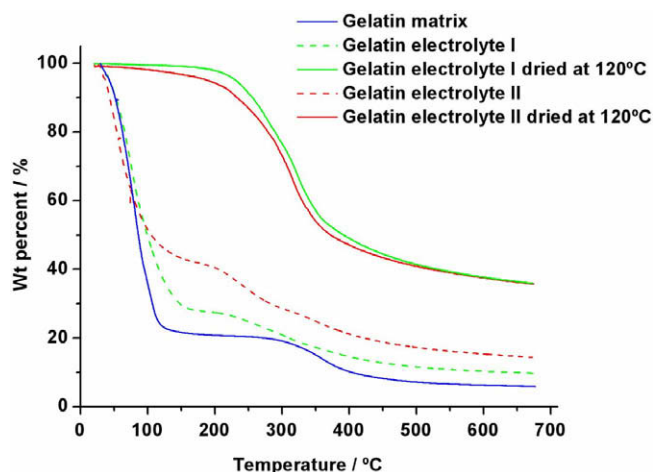


Fig. 1. TGA results of selected gelatin electrolyte.

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