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Ion-Conducting Membranes Based on Gelatin and Containing LiI/I_2 for Electrochromic Devices

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Ionic conducting membranes of gelatin plasticized with glycerol and containing LiI/I_2 have been obtained and characterized by X-ray diffraction measurements, UV-Vis-NIR spectroscopy, thermal analysis and impedance spectroscopy. The transparent (80–90% in the visible range) membranes showed ionic conductivity value of 5×10^{-5} S/cm at room temperature, which increased to 3×10^{-3} S/cm at 80°C. All the ionic conductivity measurements as a function of temperature showed VTF dependence and activation energy of 8 kJ/mol. These samples also showed low glass transition temperature of −76°C. Moreover the samples were predominantly amorphous. The membranes applied to small electrochromic devices showed 20% of color change from colored to bleached states during more than 70 cronoamperometric cycles.

Keywords Electrochromic devices; gel polymer electrolytes; gelatin; ionic conductivity

1. Introduction

In the twentieth century many synthetic polymers were considered insulating materials; however in the 1970s it was shown that polymers with conjugated double bonds, such as poly(acetylene) might have electronic conduction properties [1]. Also in the 1970s, P. Wright observed that poly(ethylene oxide) (PEO) dissolved inorganic salts and thereby could promote ionic conductivity [2]. The discovery of these two conducting polymers opened new possibilities for the use of polymers, which had been considered only insulating materials. However concerning ionic conductivity properties, the problems are due to the melting of the crystalline phase of PEO around 60°C. Therefore, modifications, such as grafting, crosslinking and plastification using other polymers, such as poly(vinyl alcohol) (PVA), poly(vinyl chloride) (PVC) and poly(difluoro vinilidene) (PVDF) have been adopted to modify the PEO matrix [3]. In recent years, environmental problems caused by waste disposal and overuse of oil have given rise to the development of new types of electrolytes specifically based on natural polymers. These natural polymer-based materials are attractive due to their availability, low cost, and biodegradation properties [4]. Polysaccharide-based electrolytes, such as hydroxyethyl cellulose, chitosan and starch have been widely studied

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[5–7]. Other natural macromolecules, like gelatin and DNA have also been investigated [8]. These ionic conducting materials are a rather complex molecular system, which contributes to the ion transport, due to the formation of a predominantly amorphous phase. In the case of gelatin, the use of crosslinking agents and plasticizers, such as formaldehyde and glycerol, respectively, improves the membrane formation properties and its plasticity as well as the adhesion to the electrodes. Therefore, this modification leads to an increase in the ionic conductivity values and mechanical strength of the electrolyte [9–14]. Aiming to insert ionic conducting species, as cations, inorganic salts are also added to the electrolyte formulation. In the case of solid polymer electrolytes, cations are coordinated with the electrons of heteroatoms present in the polymer structure [2]. According to Vieira et al. [15], electrolytes with protonic conductors present better dynamic ion transport when compared to electrolytes with alkali metal salts. Also according to the literature, the salts that provide the best conductivity for polymer electrolytes are those that release lithium ions, such as $LiClO_4$ or $LiBF_4$ [16]. Recent studies on gelatin-based electrolytes containing $LiClO_4$ or $LiBF_4$ have provided the ionic conductivity values of 1.45×10^{-5} S/cm [13].

Electrochromic materials have the property of changing color when either a voltage is applied across the material or a current passes through it. This color change should be reversible when the polarity of either the voltage or the current is reversed. Devices made with these materials are promising to the efficient use of energy. They can control the flow of light and heat passing by glazing the surface of buildings, vehicles, trains, aircrafts and etc. [17] and are also used as automotive rearview mirrors [18,19]. Different electrochromic devices have also been reported with electrolytes based on natural polymers [20]. The good results of electrochemical cycling and stability have made it possible to prepare the natural polymer-based electrolytes for other electrochemical device applications, as for example, solar cells or batteries. Depending on the device, other ionic conducting species are required. The present paper reports on the preparation and characterization of polymer electrolytes based on gelatin and containing LiI/I_2 as possible candidates for use in electrochemical devices. The characterization of small ITO/WO_3/gelatin-LiI-I_2/CeO_2-TiO_2/ITO devices using spectroelectrochemical measurement is also reported.

2. Experimental

2 g of colorless and tasteless gelatin (Dr. Oetker®) were mixed with 15 mL of Millipore Milli-Q water with controlled resistivity of 18 $m\Omega^{-1}$ cm^{-1} at 25°C, until complete dissolution. The polymer electrolyte was prepared by adding glycerol as a plasticizer, formaldehyde as a crosslinking agent and $LiI.2H_2O/I_2$ at a ratio of 10:1 w/w. Table 1 shows the composition of the samples.

The ionic conductivity measurements were performed placing 2 cm round and 5 μm thick membranes between two mirror-polished stainless steel electrodes attached to a Teflon® electrochemical cell. The conductivity values were obtained in vacuum by electrochemical impedance spectroscopy using a Solartron SI 1260 Impedance/Gain Phase Analyzer coupled to a computer in the frequency range of 10^6 to 10 Hz with amplitude of 5 mV. All measurements were taken in triplicate.

Differential scanning calorimetry (DSC) was performed under 50 mL min^{-1} N_2 flow with TA Instruments DSC-Q100 in the −100°C to 120°C at 10°C min^{-1} heating rate.

The diffraction patterns of the membranes were obtained with a Rigaku Rotaflex diffractometer, model RU200B, power of 50 kV/100 mA, radiation of $CuK_\alpha = 1.540$ Å, and the membranes scanned within the range (2θ) of 5 to 30° at room temperature.

Table 1. Composition of samples

	Gelatin		$LiI.2H_2O$		I_2		Glycerol		HCHO	
Sample	g	wt%	g	wt%	g	wt%	g	wt%	g	wt%
G1	2	37.0	0.6	11.1	0.06	1.1	2.5	46.2	0.25	4.6
G2	2	36.2	0.7	12.7	0.07	1.3	2.5	45.3	0.25	4.5
G3	2	35.5	0.8	14.2	0.08	1.4	2.5	44.4	0.25	4.4
G4	2	34.8	0.9	15.7	0.09	1.6	2.5	43.6	0.25	4.4
G5	2	34.2	1	17.1	0.1	1.7	2.5	42.7	0.25	4.3

The UV-Vis measurements were performed with a Jasco V-630 spectrophotometer, in the range of 1000 to 300 nm with 801 points and speed of 1000 nm/min.

The infrared spectroscopics (IR) were performed using a Bomem spectrophotometer model MB-102. The GPEs also in the liquid form were deposited on silicon wafers and dried with a dryer. The machine's resolution was 4 cm^{-1} with scan number of 16 in the 4000 to 400 cm^{-1} region.

Electrochromic devices with glass/ITO/WO_3/gelatin electrolyte/CeO_2-TiO_2/ITO/glass configuration and size of 1 $\times$ 2 cm^2 were obtained by assembling the 2 pieces of coated glasses. A 1 mm thick and 10 mm large gelatin-based electrolyte membrane was glued on one of the functional coatings and 1 cm free space was left for the electrical contact. The other coated substrate was then pressed onto the first one in such a way that the two coatings faced each other inside the assembled window. A 1 cm wide Cu-conducting tape (3M) was glued to the free edge of each substrate for electrical connection. The mounted cells were then sealed with a protective tape (3M).

3. Results and Discussion

To analyze the possible mechanism of ionic conduction in the gelatin-glycerol-Li/I_2 based systems, as well as the ionic conducting stability as a function of temperature, temperature-dependent ionic conductivity measurements were performed. Fig. 1 shows the ionic conductivity values of the samples with different amounts of LiI/I_2 salt as a function of temperature. It is possible to observe a non-linear behavior indicating a VTF model for ionic conductivity movement of all samples, independently of the quantity of salt. This figure also shows that all the samples have almost the same values of ionic conductivity at room temperature, i.e., 5 $\times$ 10^{-5} S/cm. This value increases two orders of magnitude, i.e., to 3 $\times$ 10^{-3} S/cm, when the temperature reaches 80°C. The samples with larger salt quantity show lower ionic conductivity values, however all the values are almost similar. These good ionic conductivity values are probably due to the chain movement, as already observed in other studies [3,14]. Also in this case, the presence of a plasticizer possibly promotes a better separation of polymeric chains and, consequently, their more pronounced movements, as observed in the plasticized pectin-based system [21].

Aiming to investigate the VTF model of the ionic conductivity shown in Fig. 1, the samples were firstly subjected to thermal analysis to obtain their glass transition temperature (Tg) values. As seen in Fig. 2, a small baseline change can be observed at −76°C. This phenomenon can be attributed to the glass transition temperature of the ionic conducting system, which is comparable to other ionic conducting gelatin membranes [13]. A more

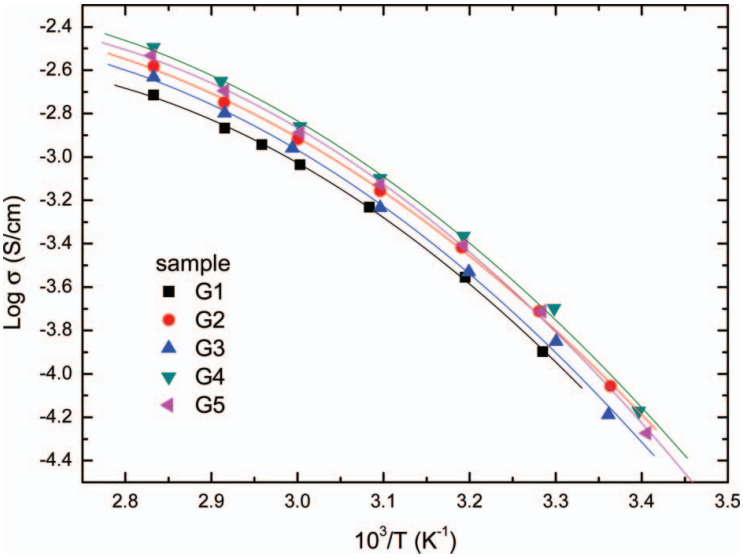

Figure 1. Log of ionic conductivity values as a function of temperature of gelatin-based electrolytes with different LiI/I_2 concentrations.

detailed analysis of all samples revealed almost the same Tg values, which are listed in Table 2.

The Tg values were then used to construct the new graph shown in Fig. 3 and following the VTF equation. Fig. 3 shows the Tg values used to construct the new graph, following

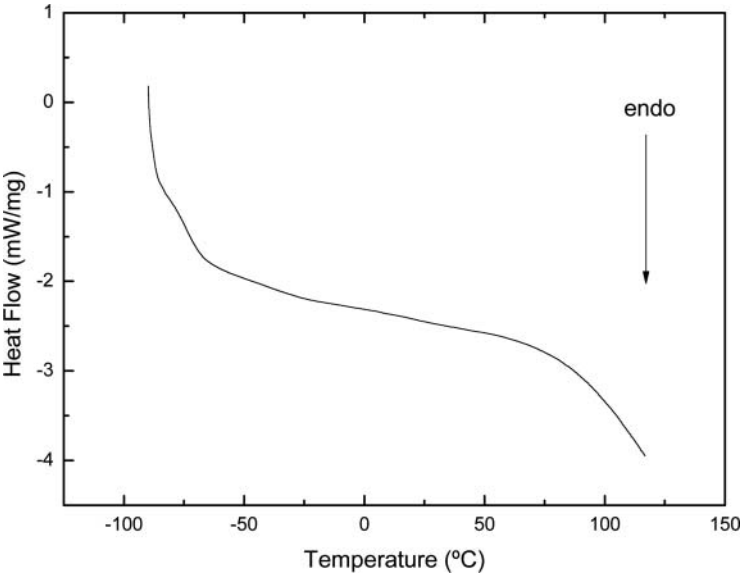

Figure 2. DSC analysis of sample G4.

Table 2. Glass transition temperature for the gelatin- based samples with different LiI/I_2 quantities

Gelatin	Tg (°C)
G1	−78
G2	−76
G3	−79
G4	−77
G5	−76

the VTF equation.

$$\sigma\,(T) = \frac{A}{T^{1/2}} \exp\left[-\frac{\Delta E}{(T - T_0)}\right]$$

Where To = Tg-50 K and E is the apparent activation energy.

According to this figure, all the results fitted linearly with the VTF model, indicating the chain movement responsible for the ions displacement. This small contribution of the polymer free volume, increased by the addition of a large amount of plasticizer can be also accountable. Moreover the larger size of this free volume increases the mobility of the polymeric chains and, consequently, improves the ionic transport [22]. These results also allowed calculating the activation energy (Ea) values, as shown in Table 3, where the same value of 8 kJ/mol for all samples can be observed again.

The increase of 11 to 17 wt% in the salt concentration of the gelatin-based samples evidenced small differences in the ionic conductivity values of around 8×10^{-5} to 10^{-4} S/cm (Table 4), different to other natural macromolecule-based gel electrolytes, in which an increase in the ionic conductivity value with the salt content is observed [15,23].

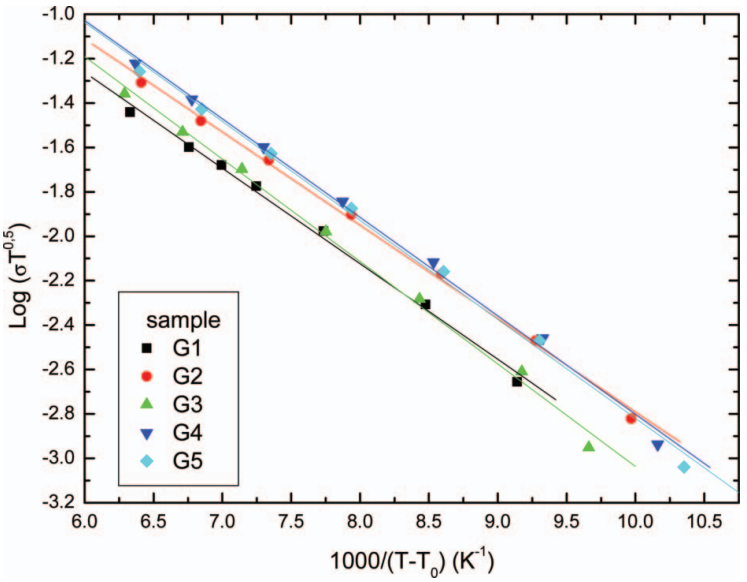

Figure 3. VTF behavior of ionic conduction for the samples based on plasticized gelatin and containing LiI/I_2.

Table 3. Activation energy values of the gelatin-based samples containing LiI/I_2

Electrolyte	Ea ($kJmol^{-1}$)
G1	8.2
G2	8.0
G3	8.8
G4	8.5
G5	8.5

Dielectric constants for the best conducting gelatin based electrolyte have been calculated from the impedance data using equation [24]

$$\varepsilon_R = \frac{Z_I}{\omega C_0 \left(Z_R^2 + Z_I^2\right)}$$

Here C_0 and f is free space permittivity and frequency. Z_R and Z_I are the real and imaginary parts of the complex permittivity. Fig. 4 shows the plot of dielectric constant as a function of frequency for gelatin-LiI electrolyte at all studied temperatures. As temperature increases, the dielectric constant values increase indicating there is increment in the number density of charge carriers in the sample. At the low frequency region, the electrode polarization can cause high accumulation of charges at the electrolyte-electrode interface, hence contributing to the rapid increases in dielectric values. Since the dielectric constant is made up of the charges, the higher dielectric constant value and the higher charge carrier density are present in the space charge accumulation area. The values of dielectric constant decrease in the high frequency region. This observation can be correlated to the increase of the periodic reversal of the electric field at the electrolyte-electrode interface with increasing frequency. The higher charge accumulation reduces the mobility of ions, thereby decreasing the dielectric constant values.

Figure 5 shows real and imaginary parts of conductivity as a function of frequency at various temperatures for the highest conducting gelatin electrolyte. The effect of temperature on the conductivity is revealed by the increased of plateaus level in the real part of conductivity (σ'). These plateaus are equivalent to direct current conductivity (σ_{DC}) values in the studied sample. When the sample is subjected to a higher temperature condition, more ions can be transported, contributing to conductivity hence the conductivity is increased. The conductivity-frequency plot showed decrease trends in its values at the low frequency region below the σ_{DC} plateaus, which is due to the electrode polarization effect [25]. This

Table 4. Ionic conductivity of the gelatin gel electrolytes as a function of LiI/I_2 concentration

Sample	$LiI.2H_2O$ (%)	σ (S/cm)
G1	11.1	7.7×10^{-5}
G2	12.7	6.4×10^{-5}
G3	14.2	8.8×10^{-5}
G4	15.7	9.8×10^{-5}
G5	17.1	7.9×10^{-5}

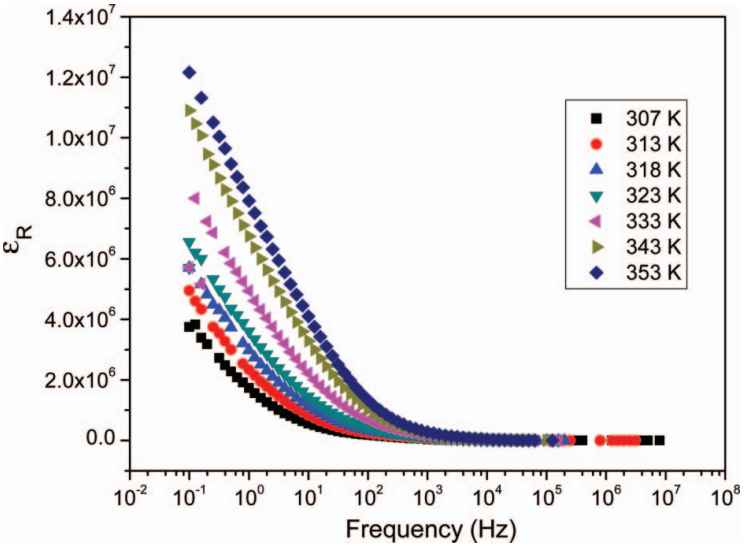

Figure 4. Dielectric constant as a function of frequency at various temperatures for the highest conducting gelatin electrolyte (G4).

statement is supported by the peak present in the imaginary part of the conductivity profile. The peak frequency shifts to higher values with the increase of temperature and the same frequency shift manner in σ_{DC} is observed.

Polymer electrolytes are developed to substitute liquid electrolytes in several electrochemical devices. For most of these devices a very interesting feature is transparency, which is easily obtained with liquid electrolytes, but not as easily with solid ones. However, some polymer electrolytes, particularly those based on natural polymers, can be obtained in thin membrane forms with very good transparency in the visible range of electromagnetic spectrum [26]. Also, as observed in Fig. 6, gelatin-based ionic conducting membranes show the optical transmittance in the 200–1100 nm range, which increases according to the wavelength from zero in the UV region at 280 nm to 89%, depending on the sample in the Vis-NIR region. As observed in this figure the transmittance values of 85% were obtained for samples G1, G2 and G5, and the transmittance values of 80% for samples G3 and G4. This difference may be due to the LiI/I_2 quantity in the sample. Also, it can be stated that the sample transparency depends on the ionic conducting species, i.e., salt or acid type and also on the plasticizer quantity. As there is no coloration and no band around 110 cm^{-1} in Raman spectrum (not shown here) [27,28] the addition of I_2 probably promotes an increase of colorless I^- species, which can contribute to the ionic conductivity values. Moreover, these good transparency results of up to 1100 nm are very similar to those of other SPEs samples based on gelatin and containing acetic acid [15] or $LiClO_4$ [14], or chitosan-based samples [29].

The IR spectroscopic analyses of gelatin-based membranes (Fig. 7) exhibited an intense and very large absorption of OH stretching in the 3300–2500 cm^{-1} region, which is probably due to the stretching vibration of glycerol hydroxyl groups and adsorbed moisture molecules. A gelatin NH bending is also observed in this region. Another characteristic peak of the glycerol molecule is situated around 1033 cm^{-1} [30]. The bands at 2936 cm^{-1} and 2875 cm^{-1} can be attributed to the stretching vibration of the CH group of the protein. The

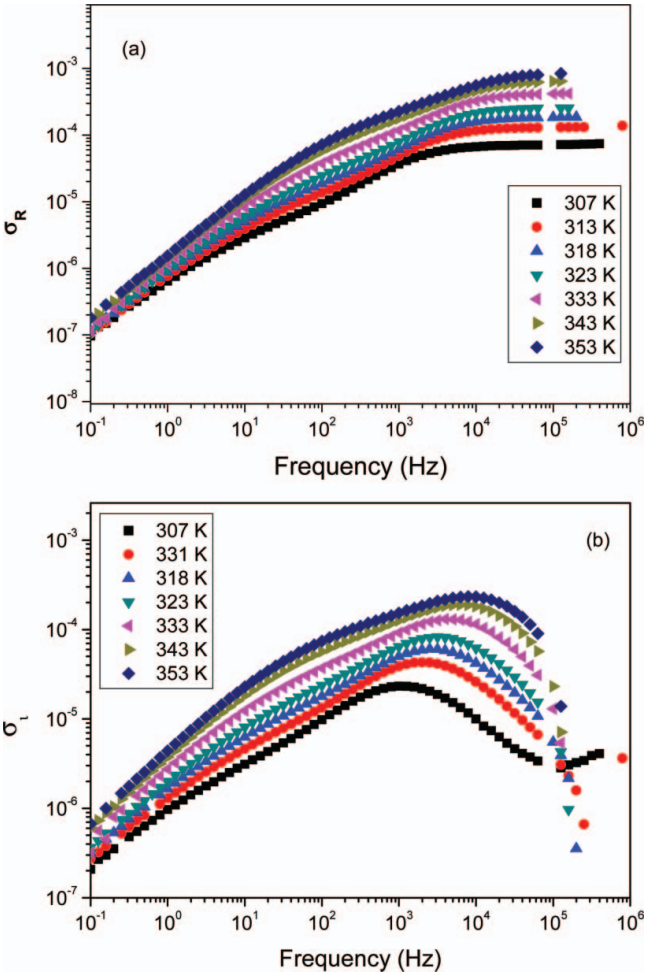

Figure 5. Real (a) and imaginary (b) parts of conductivity as a function of frequency at various temperatures for the highest conducting gelatin electrolyte (G4).

band at 3280, 1657 and 1544 cm^{-1} can be attributed to free water or amides III, I and II, respectively [30]. The band at 1657 cm^{-1} corresponds to a strong CO stretching of amide I. The 1544 cm^{-1} band can be attributed to a weak NH bending and CN stretching of amide II and the band at 1236 cm^{-1} to a weak CN stretching and NH bending of amide II [31]. Similar results were obtained by Bergo and Sobral [30] for gelatin films plasticized with glycerol.

The gelatin-based electrolyte membranes with LiI/I_2 were used to construct small electrochromic devices with glass-ITO/WO_3/gelatin GPE/CeO_2-TiO_2/ITO-glass configuration. The cyclic voltammograms of this ECD measured during the 10th and 70th cycles are shown in Fig. 8. A large cathodic peak is observed at -1.5 V and an anodic one at 0 V. For the first 50 cycles there is also a small shoulder at 0.8 V associated with another oxidation process, probably due to the LiI/I_2 used for the electrolyte preparation. It should also be stated that these voltammograms are different when compared with those obtained for ECDs composed of WO_3/gelatin-acetic acid GPE/CeO_2-TiO_2 [20] and

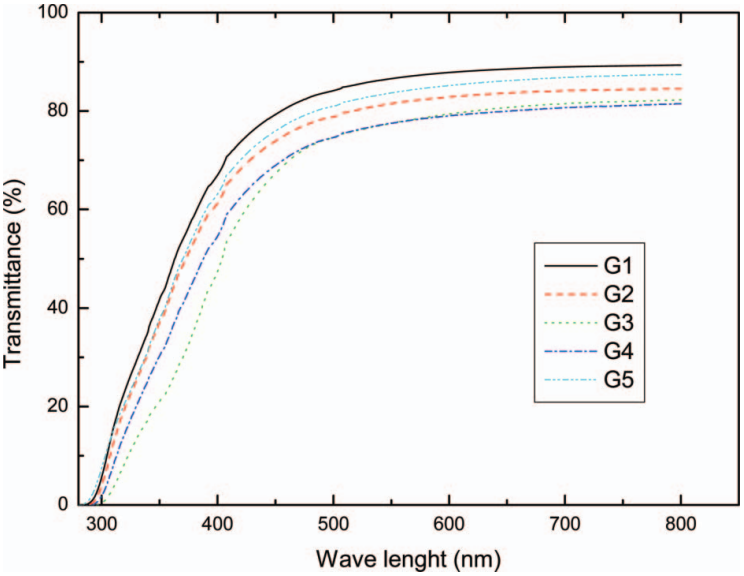

Figure 6. UV-vis spectra of the gelatin-based samples containing LiI/I_2; (G1–G5).

WO_3/starch-glycerol/CeO_2-TiO_2 [15]. The shape of the waves does not change drastically under cycling, but the current peaks are slightly displaced to positive values.

Figure 9 shows the charge density response measured by chronoamperometry (+/− 1.5 V, 15 s) of ECD containing gel electrolyte based on gelatin as a function of time for cycles 10 to 70. The insertion process (coloration) is fast. For instance, for the 30th cycle, the inserted charge at −1.5 V reaches −3 mC/cm^2 in 5 s, and this value increases up

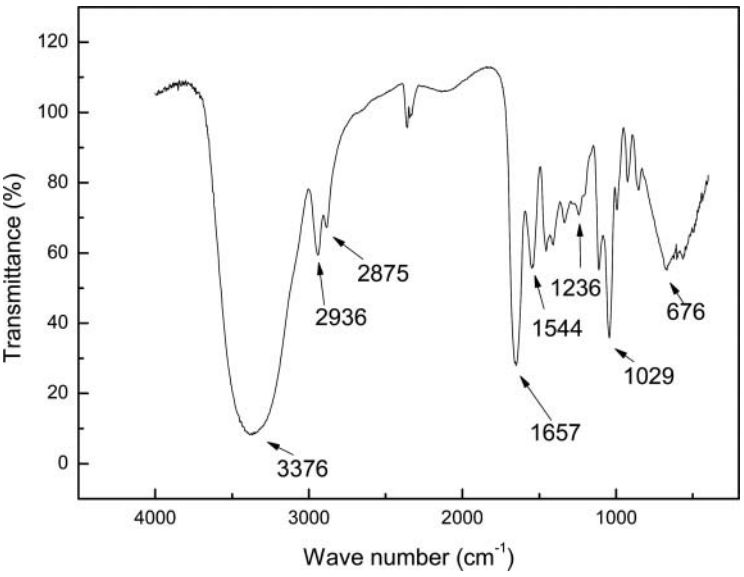

Figure 7. FTIR spectrum of the gelatin-based electrolyte; sample G4.

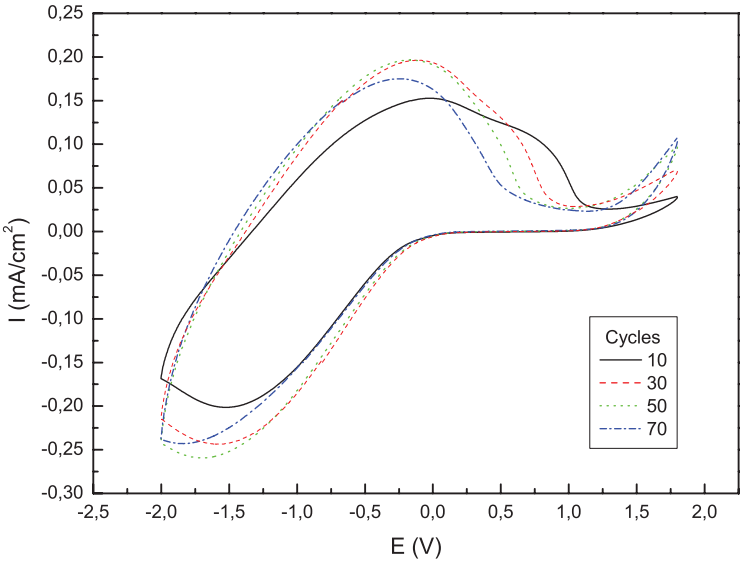

Figure 8. Cyclic voltammograms for ECD with WO_3/gelatin-electrolyte/CeO_2-TiO_2 configuration measured from the 10th to the 70th cycles.

to -4 mC/cm^2 in the next 10 s for the cycles. The best charge density value is observed for the 50th cycle, in which -4.5 mC/cm^2 is achieved in 15s of the applied potential. For the 70th cycle a reduction to -4.2 mC/cm^2 is observed.

The charge extraction occurs faster and the ECD is already transparent after applying $+1.5$ V potential for 2s. This extraction is comparable to other ECDs containing

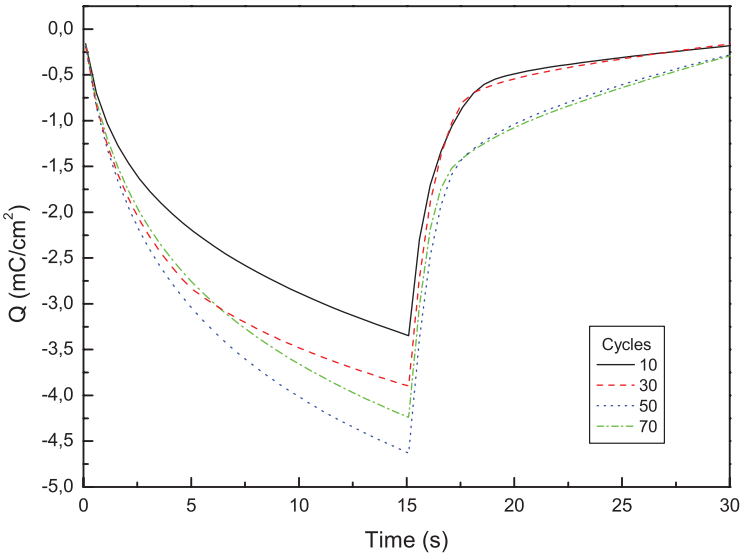

Figure 9. Charge density measured during 10 to 70 cycles for ECD with WO_3/gelatin-electrolyte/CeO_2-TiO_2 configuration.

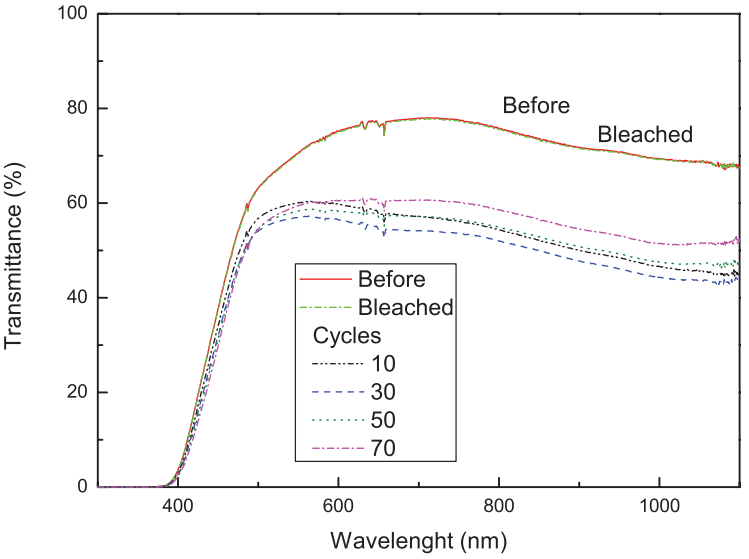

Figure 10. UV-Vis-NIR spectra for ECD composed of WO_3/gelatin-electrolyte/CeO_2-TiO_2 measured during cycles 10 to 70. The ECD was polarized for 60s at −1.5 V for the colored state and 60s at +1.5 V for the bleached one.

gelatin-based electrolytes [20]. However in the present case it is possible to observe a complete extraction of all inserted charge. Also, whenever the devices become transparent, a change in the charge extraction shape occurs from the 50th to the 70th cycles. This phenomenon is probably due to the other reaction linked to the electrolyte nature and can be seen in the voltamogramms (Fig. 8).

Figure 10 shows the UV-Vis spectra of ECDs in the 300–1100 nm range for the 10th to 70th cycles. The windows present a transmittance change of 20% between the bleached (74%) and colored states (54%) at the wavelength of 600 nm during the 30 chronoamperometric cycles. At 800 nm this difference is approximately 25%, changing from 75% in the transparent state to 50% in the colored state, similar to the other ECD with gelatin-based electrolyte [20]. For higher wavelengths, the difference between the colored and bleached states remains the same up to 1100 nm. These results are comparable to ECDs containing starch-based electrolytes with lithium ionic conductivity [32], and to ECDs built with other polymer electrolytes listed by Heusing and Aegerter [33].

4. Conclusions

Polymer electrolytes based on commercial gelatin crosslinked with formaldehyde, plasticized with glycerol and containing LiI/I_2 were obtained and characterized. The samples showed the best ionic conductivity values of 5×10^{-5} S/cm at room temperature. These values increase two orders of magnitude achieving 3×10^{-3} S/cm at 80°C. Moreover, all the samples in the membrane form were predominantly amorphous with good transparency of 80 to 90% in the visible region of the electromagnetic spectrum. The ionic conductivity values as a function of temperature indicated that the displacement of ions depends on the macromolecular chain movement, i.e., the VTF-type mechanism of ionic conductivity. DSC thermal analysis showed a low glass transition temperature of −76°C

and the VTF fitting exhibited the activation energy of 8 kJ/mol. The membranes applied to small electrochromic devices showed a 15 s coloring process achieving -4.5 mC/cm^2 in the 30th cronoamperometric cycle. The extraction process is reversible and occurs in 2 s. The transmittance value at 600 nm changes 20%, i.e., from bleached at 74% to colored at 54%, and for a higher wave length this value increases to 25%. This new type of gelatin gel electrolytes can be considered promising candidates to be used in electrochromic devices.

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