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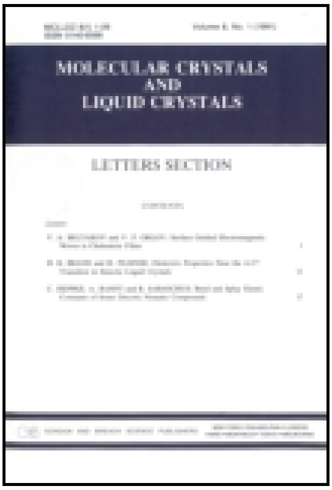

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The Influence of Glycerol and Formaldehyde in Gelatin-Based Polymer Electrolytes

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In the present work, one host natural matrix – gelatin – has been doped with magnesium triflate ($Mg(CF_3SO_3)_2$). Using gelatin as host polymer and magnesium triflate as salt, thin films were produced by varying the amount of glycerol and formaldehyde. The behavior of the samples produced was evaluated using techniques such as thermal analysis (thermogravimetric analysis – TGA and differential scanning calorimetry – DSC), complex impedance spectroscopy, and electrochemical stability. The electrolyte films produced were obtained as transparent and amorphous samples with encouraging electrochemical and thermal properties.

Keywords Gelatin; natural macromolecules; polymer electrolytes

1. Introduction

Polymer electrolytes distinguish themselves from other such materials in that they combine ionic conductivity in the solid state with mechanical flexibility, making them ideal replacements for liquid electrolytes in electrochemical cells because of their ability to form good interfaces with solid electrodes [1]. For a material to be used as a solid polymer electrolyte, it must have certain properties, such as [2]: suitable conductivity for practical devices; low electronic conductivity; good mechanical properties; chemical, electrochemical, and photochemical stability; and easy processing.

Typically, a solid electrolyte contains: a salt, one or two host polymers (called blends when it uses two polymers [3]), a plasticizer, and a crosslinking agent.

Initially, the researchers used lithium salts to produce polymer electrolytes [4]. However, other electrolytes based on salts such as magnesium and zinc triflate have emerged as good alternatives [5,6]. We must give emphasis to the preparation of materials incorporating Mg^{2+} ions as they are of utmost interest, since these materials may find use as polymer electrolytes in advanced solid state rechargeable magnesium batteries [7–10]. Magnesium (Mg) appears to be a good alternative to Li because it is positioned next to this ion in the electrochemical series and has good electrochemical performance. Also, Mg has several advantages with respect to Li: (1) Unlike Li, the resources of which are limited and localized, Mg raw resources are abundant; and as a consequence, Mg is cheaper than Li; (2) It is nontoxic and hence environmental friendly; (3) As it is less reactive than Li toward oxygen and water, it may be handled safely in open air and hazards are minimal; (4) The ionic radii

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*Address correspondence to M. Manuela Silva, Centro de Química, Universidade do Minho, Gualtar 4710057, Braga, Portugal. Tel.: +351 253 604058; Fax.: +351 253 604058. E-mail: nini@quimica.uminho.pt of Li^+ and Mg^{2+} are comparable in magnitude, meaning that Mg-based batteries may use insertion compounds that have already been developed for Li cells [11].

The first solid polymer electrolytes most studied are based on polyethylene oxide (PEO) like polymer, complexed with different salts. Currently, the synthesis of films based on natural polymers such as agar [12], gelatin [13], chitosan [14], and starch [15] is attracting interest as these films have several advantages including that they are biodegradable materials that allow one to prepare a film with appropriate properties [16]. Gelatin is a soluble protein compound obtained by partial hydrolysis of collagen, the main fibrous protein constituent in bones, cartilages, and skins. Therefore, the source, age of the animal, and type of collagen, are all intrinsic factors influencing the properties of the gelatins [17]. This biomaterial has been extensively studied due to its ability to form films, a property that makes it of potential interest for a lot of applications, such as, emulsifiers, foaming agents, colloid stabilizers, fining agents, biodegradable packaging materials, and microencapsulating agents [17].

In polymers, on one hand, the addition of high levels of salt causes an increase in the conductivity and, on the other hand, is known to increase the glass transition temperature (T_g). In order to lower the T_g, thus increasing the segmental motion of the polymer and therefore the ionic conductivity, plasticizers have been added to the synthesis of electrolytes [18]. Many organic molecules can be used as plasticizers but due to the mechanical properties and transparency glycerol is the most appropriate [19]. There are a large number of articles describing the effects of plasticizers on the physical, chemical, and functional properties of biodegradable films. The addition of plasticizers helps to decrease inherent brittleness of gelatin films by reducing intermolecular forces, thus increasing the mobility of polymeric chains and improving their flexibility [20].

To improve the functional properties of polymeric films, crosslinking agents such as formaldehyde, glutaraldehyde, or glyoxal [21] are added. Formaldehyde is flammable and colorless, with a pungent odor at room temperature. Epidemiological studies classify formaldehyde as a carcinogen, so one should avoid prolonged exposure to this compound [22].

In this work, electrolytes with gelatin and magnesium triflate were produced. We also studied the effect of the amount of glycerol added as well as the absence of formaldehyde in the compositions.

2. Experimental

2.1. Solid Polymer Electrolyte

The polymer electrolytes (Fig. 1) were prepared, according to the procedures present in the literature [23–26]. Samples of gelatin and magnesium triflate were prepared by dispersion of 2.00 g of commercial colorless gelatin (Vahiné) in 15 mL of ultrapure water (Milli-Q) and heated under magnetic stirring for a few minutes up to 50°C for complete dissolution. After this, the following were added: glycerol, 0.50 g or 1.25 g (Himedia, 99.5%); formaldehyde, 0.25 g or 0.00 g (Panreac, 37–38%); and 0.25 g of magnesium triflate (Aldrich, 99%). The resulting solutions were then poured on Petri plates and cooled at room temperature and then dried in a Büchi oven between 60°C and 90°C, for 96 h, to form transparent membranes. In Table 1, the relevant details of the synthetic procedure of the samples are presented.

2.2 Measurements

2.2.1. Thermal Analysis. Polymer electrolyte sections were removed from dry films and subjected to thermal analysis under a flowing argon atmosphere between −60°C and 120°C

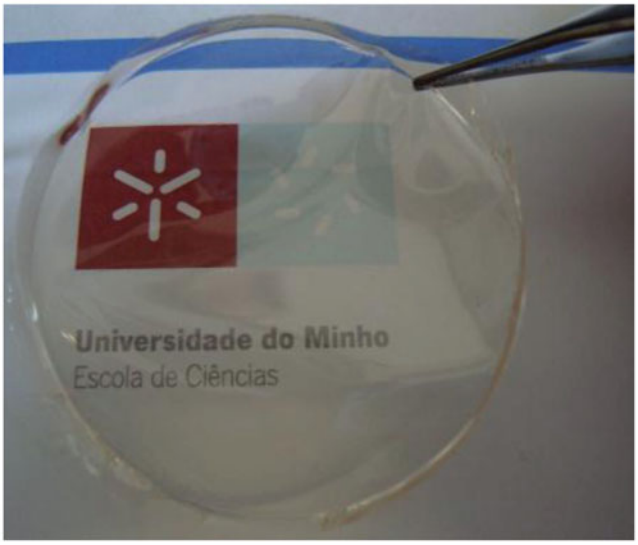

Figure 1. Physical appearance of a sample.

and at a heating rate of 5°C min^{-1} using a Mettler DSC 821e. Samples were transferred to 40 μL aluminium cans with perforated lids within a dry argon-filled glovebox. Samples for thermogravimetric studies were prepared in an identical manner, transferred to open platinum crucibles, and analyzed using a Rheometric Scientific TG1000 thermobalance operating under a flowing argon atmosphere with temperatures between 30°C and 700°C. A heating rate of 10°C min^{-1} was used with all the samples.

2.2.2. Impedance Spectroscopy. The total ionic conductivity of the gelatin electrolytes 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/gelatin electrolyte/electrode assembly was placed in a suitable constant volume support and installed in a Büchi TO51 tube oven with a type K thermocouple localized close to electrolyte disk to measure the sample temperature. Bulk conductivities of electrolyte samples were obtained with Schlumberger Solartron 1250 frequency response analyzer during heating cycles between 25°C and 100°C and at approximately 7°C intervals.

Table 1. Relevant details of the synthetic procedure of the samples

Sample	m_{gelatin} (g)	m_{glycerol} (g)	$m_{\mathrm{formaldehyde}}$ (g)	m $Mg(CF_3SO_3)_2$ (g)
Matrix	2.00			–
S1		0.50	0.25	0.25
S2			–	
S3		1.25	–	

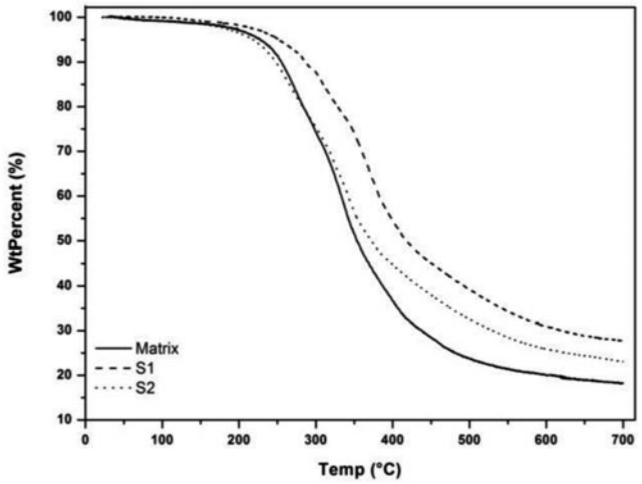

Figure 2. Comparison of TGA curves of the compositions with and without formaldehyde.

2.2.3. Electrochemical Stability. Evaluation of the electrochemical stability window of electrolyte compositions was carried out under dry argon using a two-electrode cell configuration. The preparation of a 25-μm-diameter gold microelectrode surface, by the conventional polishing routine, was completed outside the drybox. The microelectrode was subsequently washed, dried, and transferred to the drybox. The cell assembly was initiated by locating a clean lithium disk counter electrode (Aldrich, 99.9%, 10 mm diameter, 1 mm thick) on a stainless steel current collector. A thin-film sample of electrolyte was placed over the counterelectrode and the cell assembly was completed by locating and supporting the microelectrode in the center of the electrolyte disk. The assembly was held together firmly with a clamp and electrical contacts were made to the Autolab PGSTAT-12 (Eco Chemie) used to record voltammograms at a scan rate of 30 mV s^{-1}. Measurements were carried out at room temperature within a Faraday cage located inside the measurement glovebox.

3. Results and Discussion

3.1. Thermal Behavior of Electrolytes

Thermal stability of gelatin-magnesium-based electrolytes was studied by thermogravimetric analysis. Figure 2 shows that the sample without formaldehyde is the least stable, when compared with the matrix and the sample containing formaldehyde. On the other hand, even without the formaldehyde, the sample has a value of thermal stability above 200°C, which is a value considered acceptable for use in commercial devices. The TGA curves collected in Fig. 2 indicate that the presence of the guest magnesium triflate salt does not appear to destabilize significantly the host structure in a nonoxidizing atmosphere.

In Fig. 3, the results obtained for the samples with different quantities of glycerol are presented. An increase in the amount of glycerol makes the sample less stable because the onset temperature decreases. According to some authors the explanation may be in the fact that the plasticizer causes a decrease in intra- and intermolecular interactions and so the degradation process is facilitated [27].

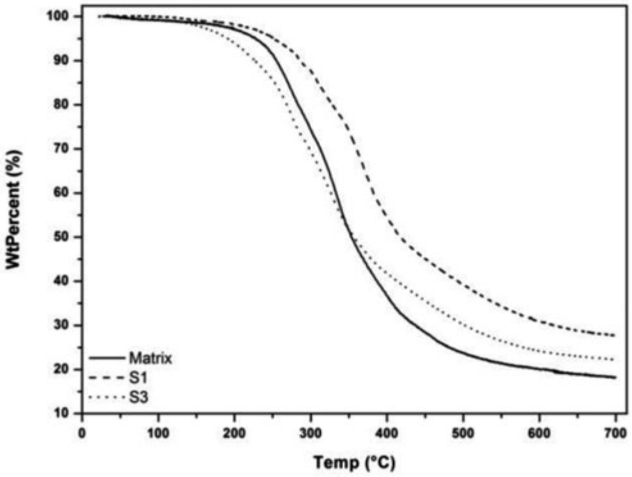

Figure 3. Comparison of TGA curves of the compositions with different amounts of glycerol.

In all cases, the degradation process occurs in one stage due to different interactions between the polymer and magnesium triflate salt. From Figs. 2 and 3, we can observe a very accentuated weightloss of almost 80%, above 180°C due to the degradation process. In the case of gelatin-based samples, this process occurs in one stage upto 400°C, and slowly continues as the temperature is increased upto 700°C. The remaining residue was 20% in mass of the starting material for matrix and 25%–30% for the other samples. The same behavior is observed in other polymer electrolytes based on gelatin and lithium salts [28,29].

From the results of Figs. 2 and 3, we can see that the samples have no water. At this point, it should be stated that even glycerol is a hydrophilic substance and its presence does not promote water; when compared with agar-based electrolytes with less amount of

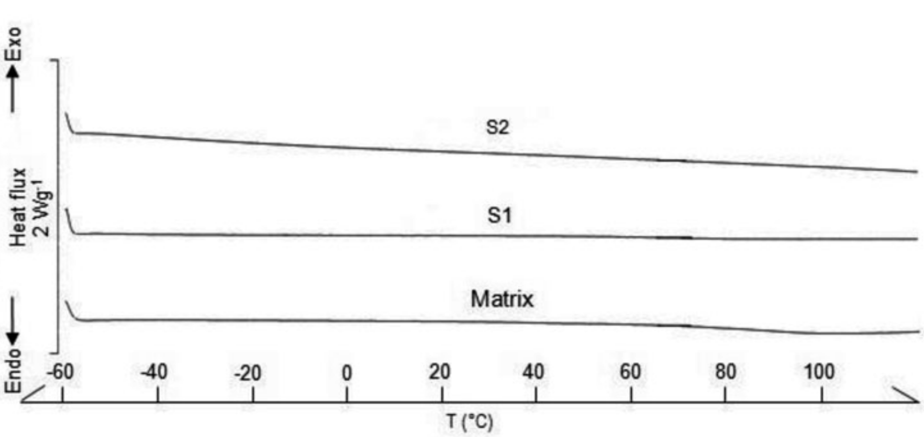

Figure 4. DSC analysis of the compositions with and without formaldehyde.

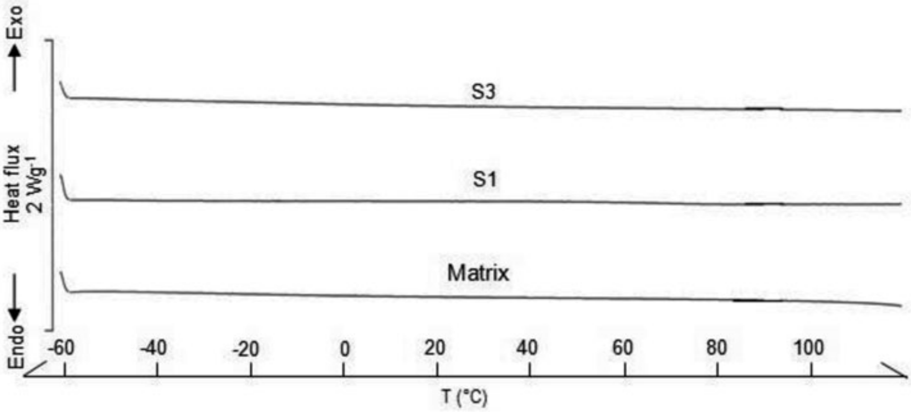

Figure 5. DSC analysis of the compositions with different amounts of glycerol.

glycerol, an increased water absorption capacity of the film is observed for other natural polymer electrolyte-based membranes [30].

DSC traces of the gelatin-based electrolytes are shown in Figs. 4 and 5. The DSC measurements were performed in the –60°C to 120°C range of temperature and no glass transition temperature was detected within this range. It was possible to conclude that all study compositions are predominantly amorphous and, on the other hand, we can say that the addition of more glycerol and the default of formaldehyde do not promote changes in the samples. These thermal analyses show very similar behavior when compared with other gelatin-based electrolytes [31,32] and are therefore considered acceptable for most applications under normal operating conditions.

3.2. Impedance Spectroscopy

The ionic conductivity as a function of temperature measurements of the gelatin-based electrolytes is included in Figs. 6 and 7.

A very important parameter was to verify the effect of the absence of formaldehyde on ionic conductivity (Fig. 6). Data presented in Table 2 show that the ionic conductivity values are very similar to the compositions studied. This proximity of values suggests that it is not necessary to add formaldehyde to gelatin electrolytes.

The conductivity study of the samples with different amounts of glycerol (Figure 7) shows that the increased amount of glycerol results in an increase in conductivity.

Other researchers have studied the influence of glycerol in gelatin electrolytes containing $LiBF_4$ [22]. They concluded that the increase of plasticizer promoted greater mobility

Table 2. Ionic conductivity and values of E_a

	σ / S cm^{-1} ($T = 25$°C)	σ / S cm^{-1} ($T = 95$°C)	E_a/KJ mol^{-1}
S1	3.80×10^{-10}	1.70×10^{-6}	49.0
S2	2.18×10^{-10}	1.12×10^{-6}	49.4
S3	1.26×10^{-10}	1.50×10^{-5}	40.5

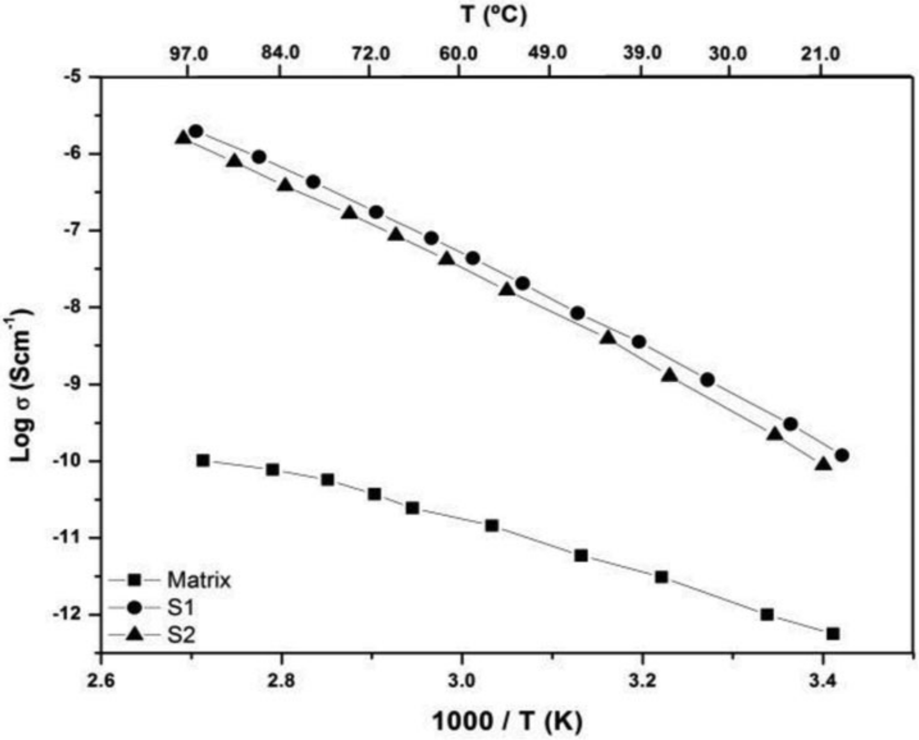

Figure 6. Ionic conductivity of gelatin electrolytes with and without formaldehyde.

of ions due to better solvation of the lithium ion. On the other hand, as the electrolyte is more malleable, it promotes a decrease in intra- and intermolecular interactions in the plasticizer and gelatin induced by hydrogen bonding of OH groups of glycerol with the chains of amino acids. As expected, the incorporation of more glycerol into the matrix increases the ionic conductivity over the entire temperature range investigated. The temperature dependence of the ionic conductivity was well described by the Vogel–Tamman–Fulcher (VTF) equation in the temperature range from 25°C to 100°C. The VTF expression implies that the main mechanism of ion conduction can be related to the free volume theory. The fitted values of E_a for different polymer electrolytes are shown in Table 2. The fitted values of E_a decrease with the addition of glycerol. This is in agreement with the fact that the energy barrier to the ion transport decreases, leading to a decrease in the activation energy.

The levels of ionic conductivity observed with the electrolytes proposed here are modest. The conductivity of these systems is too low for room temperature performances; however, it could be interesting to investigate this system as a new electrolyte for superambient applications.

3.3. Electrochemical Stability

The electrochemical stability range of the gelatin-based electrolyte (S_3) was determined by microelectrode cyclic voltammetry over the potential range between –1.0 V and 9.0 V

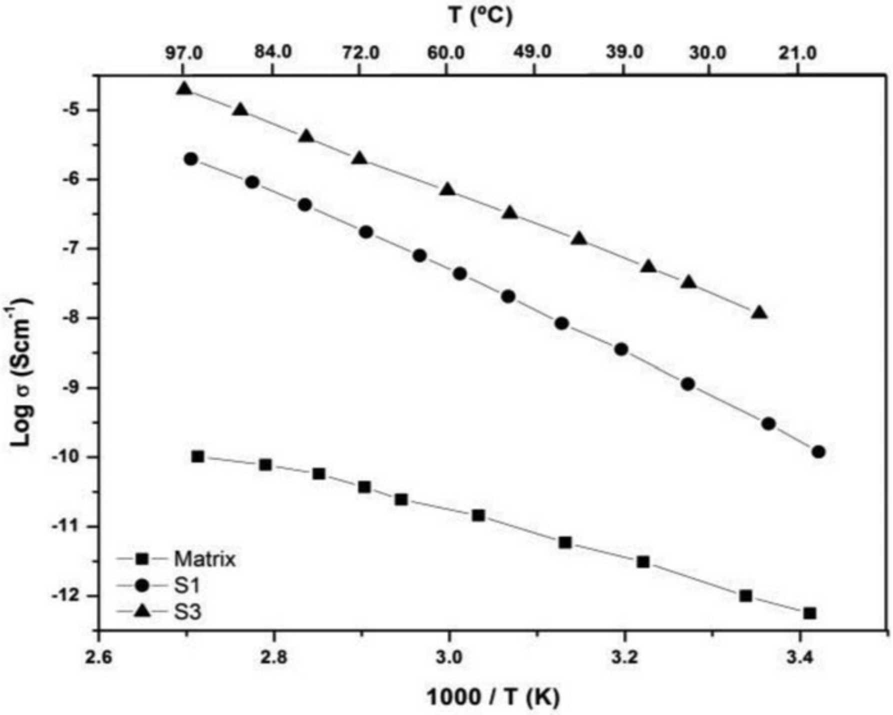

Figure 7. Ionic conductivity of gelatin electrolytes with different amounts of glycerol.

versus a lithium-reference electrode, at 30 mV s^{-1}, and at ambient temperature (Fig. 8). The anodic current onset may be associated with the decomposition of the polymer electrolyte. Figure 8 shows good stability until 4.0 V (vs. Li/Li+) for S_3, followed by an oxidation, a value considered adequate for commercial applications.

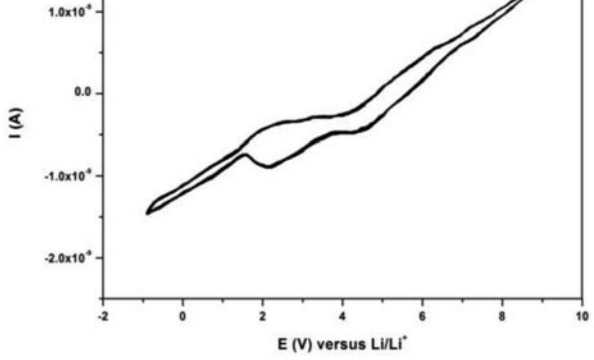

Figure 8. Cyclic voltammogram of the sample S_3 obtained at room temperature.

4. Conclusion

In this study, gelatin electrolytes were prepared in order to study the influence of formaldehyde and glycerol present in the compositions. Formaldehyde is toxic to humans and therefore it was thought to remove this component during the synthesis of electrolytes. With the analysis made, it is possible to assert that the absence of a crosslinking agent does not cause major changes in electrolytes. The most important results were obtained in terms of ionic conductivity because the values are very similar which leads us to conclude that there is no need to add formaldehyde to the compositions. In relation to the amount of glycerol added, the results were also interesting. Increasing the amount of glycerol led to obtaining more flexible films, more conductor electrolytes with electrochemical stability up to about 4.0 V, and lower thermal stability.

Acknowledgments

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