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Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and
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To cite this article: R. D. Alves, L. C. Rodrigues, J. R. Andrade, A. Pawlicka, L. Pereira, R.
Martins, E. Fortunato & M. M. Silva (2013): Study and Characterization of a Novel Polymer Electrolyte
Based on Agar Doped with Magnesium Triflate, *Molecular Crystals and Liquid Crystals*, 570:1, 1-11

To link to this article: <http://dx.doi.org/10.1080/15421406.2012.703041>

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Study and Characterization of a Novel Polymer Electrolyte Based on Agar Doped with Magnesium Triflate

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In the present work one host natural matrix – agar – has been doped with magnesium triflate ($Mg(CF_3SO_3)_2$) with the goal of developing electrolytes for the fabrication of solid-state devices. The resulting samples have been represented by the notation $Agar_nMg(CF_3SO_3)_2$, where n represents the percentage of the magnesium triflate salt proportion in the electrolyte samples. The samples investigated, with n between 0.00% and 37.56%, have been obtained as transparent and thin films. The samples have been characterized by conductivity measurements, thermal analysis, cyclic voltammetry, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The agar-based electrolytes were also tested as ionic conductor in an electrochromic device with the following configuration: glass/indium tin oxide (ITO)/ WO_3 /agar-based electrolyte/ CeO_2-TiO_2 /ITO/glass.

Keywords Agar matrix; electrochromic devices; magnesium triflate; solid polymer electrolytes

1. Introduction

Magnesium (Mg) appears to be a good alternative to lithium (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 it is cheaper than Li; (2) it is nontoxic, and hence environmentally friendly; (3) as it is less reactive than Li toward oxygen and water, it may be handled safely in open air and hazards are minimized; (4) the ionic radii of Li^+ and Mg^{2+} are comparable in magnitude, meaning that Mg-based batteries may use insertion compounds that have already been developed

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for Li cells. Aurbach et al. [1] demonstrated that the use of Mg for the fabrication of rechargeable solid-state batteries is indeed very promising. Several authors reported the synthesis and properties of conventional Solid Polymer Electrodes (SPEs) composed of poly(ethylene glycol) (PEG) and magnesium thiocyanate ($\text{Mg}(\text{SCN})_2$) [2], magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$) [2,3], or magnesium chloride (MgCl_2) [4–9].

The electrochromic materials have attracted increasing interest in the last three decades [10]. The color of these compounds may be electrochemically switched in a reversible and persistent manner (in general from a transparent or “bleached” state to a colored or “written” state). The electrochromic materials may find use in controllable light-reflective or light-transmissive devices for storage and display of optical information, anti-glare automobile rear- and side-view mirrors, sunglasses, protective eyewear for military use, aircraft canopies with controllable optical transmission, glare-reduction systems for buildings or “smart windows,” and reactive labels [11–15].

Over the last few years, commercial agar has been extensively tested in order to apply it as an electrolyte in electrochromic devices [16, 17]. Attention has been focused in the application of natural macromolecules because of their biodegradability, low production cost as well as good physical and chemical properties.

In this paper, the preparation and characterization of novel systems based on agar host matrix and magnesium triflate, as guest salt, are described.

2. Experimental

2.1 Solid Polymer Electrolyte

The polymer electrolytes (Fig. 1) were prepared according to the procedures present in the literature [16]. Samples of $\text{Agar}_n\text{Mg}(\text{CF}_3\text{SO}_3)_2$ were obtained by dispersion of 0.5 g of agar (Aldrich, Spain) in 30 mL of ultra-pure water (Milli-Q, Portugal), and heated under magnetic stirring for a few minutes up to 100°C for complete dissolution. After this, 0.5 g of glycerol (HiMedia, Spain, 99.5%) as plasticizer, 0.5 g of formaldehyde (Panreac, Spain, 37%–38%), and different quantities of salt were added under magnetic stirring (Table 1). 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.



Figure 1. Physical appearance of a sample.

Table 1. Study of Agar-Mg(CF₃SO₃)₂ Polymer Electrolyte.

Samples (Agar _n Mg (CF ₃ SO ₃) ₂)
Agar _{0.00%} Mg(CF ₃ SO ₃) ₂
Agar _{16.79%} Mg(CF ₃ SO ₃) ₂
Agar _{22.82%} Mg(CF ₃ SO ₃) ₂
Agar _{28.35%} Mg(CF ₃ SO ₃) ₂
Agar _{32.30%} Mg(CF ₃ SO ₃) ₂
Agar _{37.56%} Mg(CF ₃ SO ₃) ₂

The differential scanning calorimetry (DSC) was performed under a flowing argon atmosphere between -60°C and 120°C and at a heating rate of $5^{\circ}\text{C}/\text{min}$ using a Mettler DSC 821e (Mettler, Switzerland). Samples were transferred to $40\ \mu\text{L}$ aluminum cans with perforated lids within a dry argon-filled glove box. Thermogravimetric (TG) measurements were obtained with Rheometric (England) Scientific TG1000 thermobalance operating under flowing argon at a heating rate of $10^{\circ}\text{C}/\text{min}$.

The total ionic conductivity of the Agar_nMg(CF₃SO₃)₂ was determined by introducing an electrolyte disk between two 10 mm diameter ion-blocking gold electrodes (Goodfellow, England, $>99.95\%$) to form a symmetrical cell. The electrode/Agar_nMg(CF₃SO₃)₂/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.

The evaluation of the electrochemical stability window of electrolyte compositions was carried out under an argon atmosphere using a two-electrode cell configuration. The preparation of a $25\ \mu\text{m}$ diameter gold microelectrode surface, by polishing it with a moist cloth and $0.05\ \mu\text{m}$ alumina powder (Buehler, Spain), was completed outside the dry box. The cell was assembled by locating a clean lithium disk counter electrode (cut from Aldrich, 99.9% , $19\ \text{mm}$ diameter, $0.75\ \text{mm}$ thick) on a stainless steel current collector, and centering a sample of electrolyte on the electrode surface. A small volume ($2\ \mu\text{L}$) of tetrahydrofuran (THF) was placed on the microelectrode surface. The microelectrode was then located on the electrolyte surface and supported firmly by means of a clamp. The use of THF to soften the electrolyte was necessary to achieve a reproducible microelectrode/electrolyte interfacial contact. An Autolab PGSTAT-12 (Eco Chemie, England) was used to record voltammograms at a range of scan rates ($30\ \text{mV s}^{-1}$ and $100\ \text{mV s}^{-1}$). Measurements were performed at room temperature (25°C) and 80°C , within a Faraday cage.

The structure of the film was examined on silicon wafer by X-ray Rigaku (imported from Brazil) Utma 4 diffractometer, power of $50\ \text{kV}/50\ \text{mA}$ and Cu $K\alpha$ irradiation, speed of $2^{\circ}\ \text{min}^{-1}$, in an angle range (2θ) of 5° – 40° , at room temperature.

The scanning electron microscopy (SEM) micrographies were obtained with SEM/FIB ZEISS Auriga.

The electrochromic devices with the configurations glass/indium tin oxide (ITO)/WO₃/electrolyte/CeO₂-TiO₂/ITO/glass were obtained by assembling the two pieces of coated glasses. The electrolytes in the form of membranes were deposited on glass/ITO/WO₃ coatings, and $1\ \text{cm}$ free space was left for the electrical contact. Then, the other coated substrate 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, Brazil) was glued to the free edge of each substrate for electrical connection. The mounted cells were finally sealed with a protective tape (3 M, Brazil). The electrochemical measurements were performed with Autolab 302N with FRA 2 module (imported from Brazil), at a scan rate of 50 mV s^{-1} .

3. Results and Discussion

Thermal stability of agar–magnesium-based electrolytes studied by thermogravimetric analysis (TGA) and of all the electrolytes is similar. Figure 2 shows that the addition of salt stabilizes the matrix because the degradation temperature increases in the samples containing salt in a nonoxidizing atmosphere. This behavior is not similar to that reported for biohybrid based on poly(epsilon-caprolactone) (PCL) and magnesium triflate [18], but is similar for agar-based electrolytes with different acetic acid concentration [17]. In the region of 220°C – 400°C , a film of agar showed a very accentuated mass loss of 65%, which marks the decomposition of sample, and slowly continues as the temperature is increased up to 700°C . The remaining residue was 15% in mass of the starting materials. In the case of samples with magnesium salt, the loss mass behavior as a function of temperature is different. The degradation process occurs in two stages for the agar-based electrolytes with magnesium salt, on the basis of assumption that the negligible initial mass loss observed ($<0.5\%$ – 1.0%) is exclusively associated with the release of solvents, such as water adsorbed or coordinated. These stages are due to the agaropectin and agarose presence in the samples and the different interactions with the magnesium triflate salt. The onset

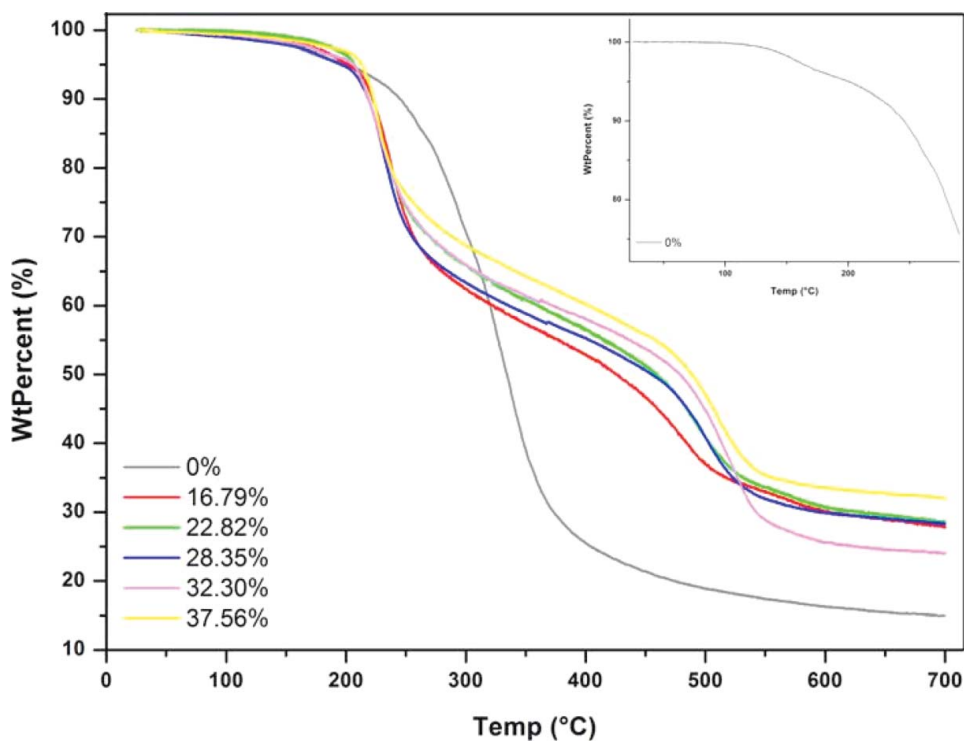


Figure 2. Thermogravimetric analysis of $\text{Agar}_n\text{Mg}(\text{CF}_3\text{SO}_3)_2$ electrolytes.

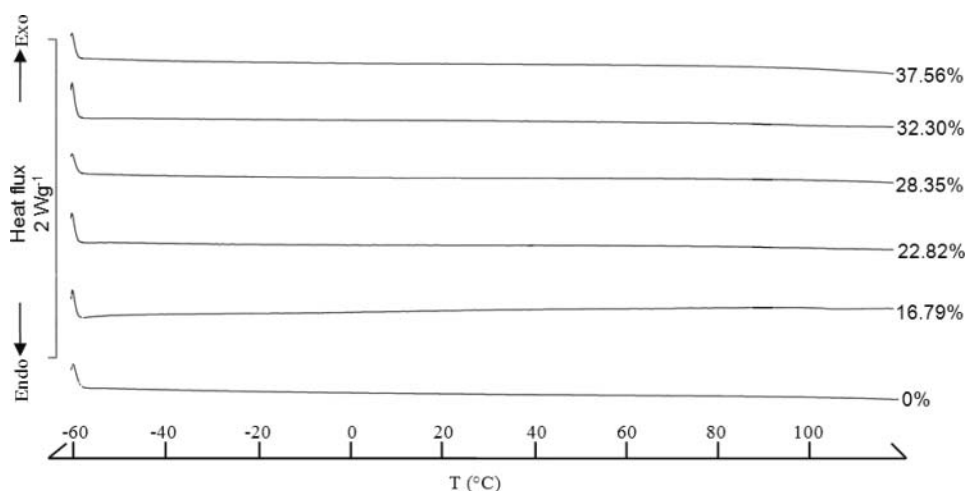


Figure 3. Differential scanning calorimetry analysis of Agar_nMg(CF₃SO₃)₂ electrolytes.

temperature of thermal decomposition was estimated by TGA using extrapolation of the baseline and tangent of the curve of thermal events to identify the initiation of sample weight loss. We may conclude that in samples with $n = 22.82\%$, 28.35% , and 32.30% the onset of thermal decomposition occurs at approximately 205°C , whereas in the case of samples with $n = 16.79\%$ and 37.56% degradation starts at about 210°C (Fig. 2). In the first stage, the samples degradation with 40% starts at 205°C – 210°C and ends at 320°C – 330°C , between 40% and 50% weight loss starts at 320°C – 330°C and slowly continues at 450°C . In the second stage, the samples degradation with 50% starts at 450°C and ends at 550°C , and slowly continues at 700°C . The remaining residue was 25% for the sample with $n = 32.30\%$ and 35% for $n = 37.56\%$. For the other electrolytes the remaining residue was 30% .

The DSC traces of the Agar_nMg(CF₃SO₃)₂ are shown in Fig. 3. 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 also possible to conclude that no crystalline peaks are observed, which suggests a total dissolution of magnesium triflate in the polymer matrix. It is expected from the information obtained by the DSC characterization that the systems have predominantly amorphous character. This behavior is similar to the one presented by gelatin network electrolyte doped with europium picrate [19].

The ionic conductivity as a function of temperature measurements of the Agar_nMg(CF₃SO₃)₂-based electrolytes are included in Fig. 4. Low lattice energy salts composed of a polarizing cation and a large anion of delocalized charge are the most adequate salts for the preparation of polymer electrolytes [20] (Mg²⁺ and CF₃SO₃⁻ ions fulfill both requirements). However, cation diffusion depends critically on the strength of the cation–polymer interaction, although strong bonds are essential for polymer electrolytes formation, labile bonds are necessary for cation mobility.

We can observe that the ionic conductivity depends strongly on many factors, such as salt concentration and temperature. The sample that exhibited more conductive is the Agar_{32.30%}Mg(CF₃SO₃)₂, and the maximum conductivity values are 1.0×10^{-6} and 3.8×10^{-5} S cm⁻¹ at 30°C and 70°C , respectively. The salt addition promotes an increase in the ionic conductivity until 32.30% , more salt added to the matrix endorses a decrease in conductivity probably due to the formations of complexes that reduces the mobility of the charge carriers.

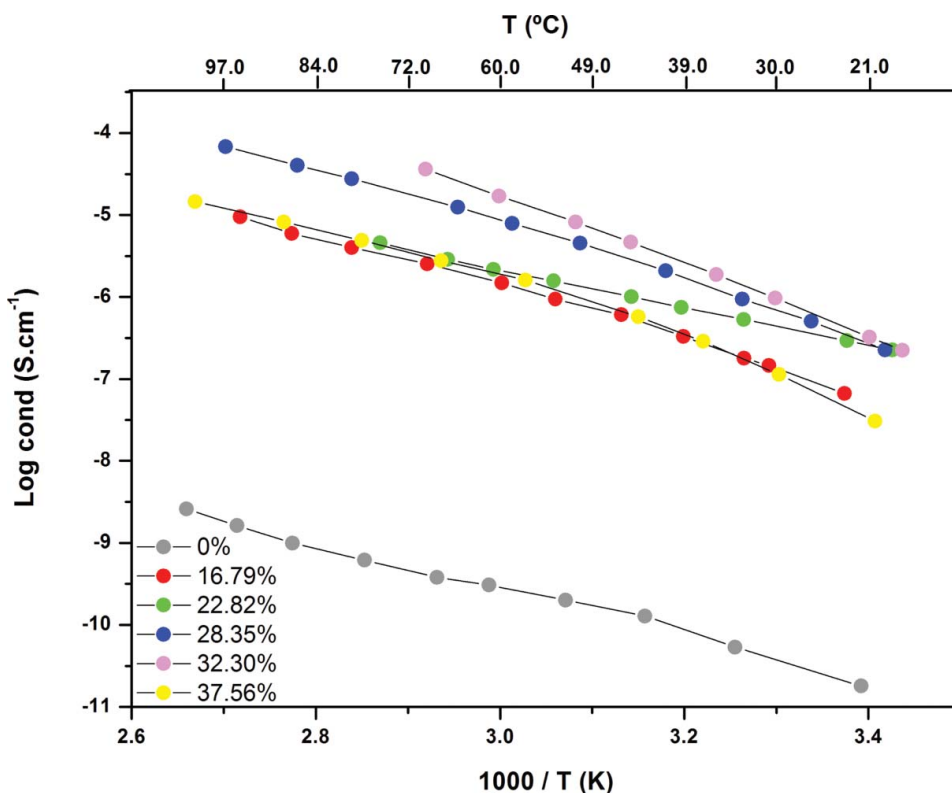


Figure 4. Total ionic conductivity of Agar_nMg(CF₃SO₃)₂-based electrolytes.

The ionic conductivity displayed by the Agar_nMg(CF₃SO₃)₂-based electrolytes may be correlated with the conduction mechanism that occurs in the agar matrix medium, which must be substantially different from that found in conventional polyethylene oxide (PEO)-based matrices. In fact, the nature of the available host matrix coordinating sites differs drastically in these types of systems, that is, ether oxygen atoms in agarose are quite different than ether oxygen atoms in PEO macromolecules. Consequently, the cation–heteroatom interaction is different, probably much more efficient in PEO than polysaccharide matrices.

The behavior for lower salt concentration may be associated with the existence of free salt. Uncomplexed salt was not detected by the DSC because the melting point of this salt is located at temperatures higher than the onset of thermal degradation. The high concentration of associated ionic species may be confirmed by spectroscopic analysis. Raman spectroscopic analyses, which are underway, will hopefully help us to elucidate the species (free ions, ion contact pairs, or charged clusters) responsible for the conductivity behavior.

The levels of ionic conductivity observed with the electrolytes proposed here are modest and are associated to both anion and cation mobilities. As already reported, the mobility of Mg²⁺ is very low due to interaction between Mg²⁺ and oxygen present in the polymer matrix [21]. Consequently, systems based on magnesium salts are expected to be essentially anionic conductors. The DC polarization measurements have demonstrated that this prediction is correct [20]. The conductivity of these systems is too low for room temperature performances; however, it could be interesting to investigate this system as a

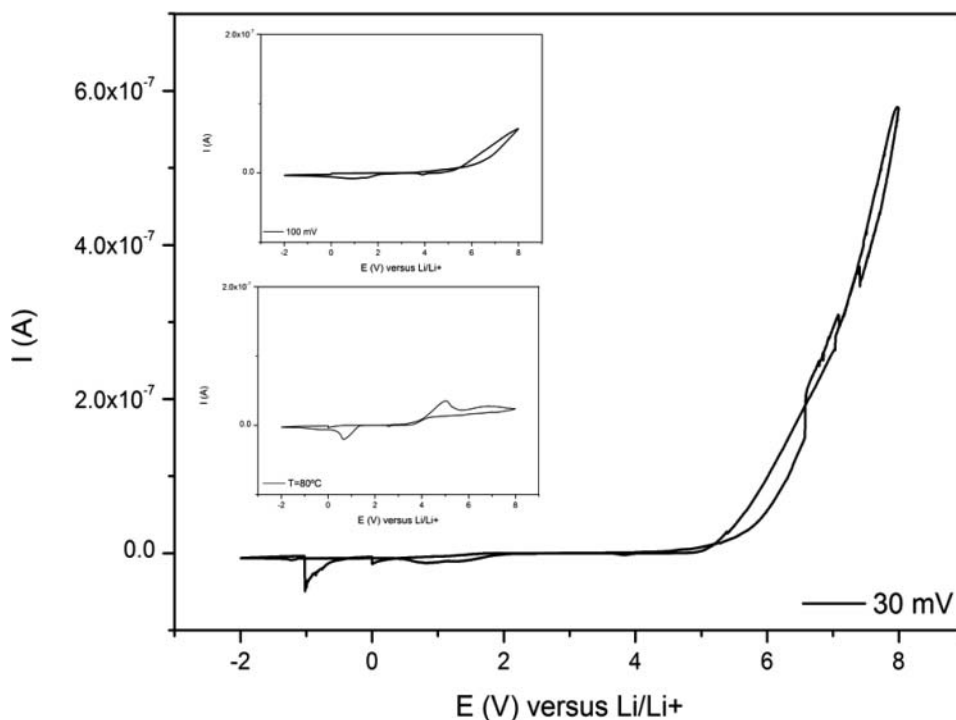


Figure 5. Voltammogram of Agar_{32.30%}Mg(CF₃SO₃)₂ electrolyte at a 25 μ m diameter gold micro-electrode versus Li/Li⁺. Initial sweep direction is anodic. Sweep rate are 30 and 100 mV s^{-1} .

new electrolyte for super ambient applications, choosing appropriated molar ratios. The SPEs must have an appropriate balance of properties if they are to be successful as device components. Also, it is important to emphasize that the system described in this paper represents materials with good performance for application in electrolytic component and the active solid-state electrochromic layer.

The electrochemical stability range of the Agar_{32.30%}Mg(CF₃SO₃)₂-based electrolyte was determined by microelectrode cyclic voltammetry over the potential range between -2.0 V and 8.0 V versus a lithium-reference electrode, at a range of scan rates (30 mV s^{-1} and 100 mV s^{-1}), at ambient temperature, and at 80°C (Fig. 5). The cathodic portion of the curve refers to the process of ion intercalation, and the anodic portion reflects the process of ion extraction out of lithium. Like other authors, also (see Ref. [22]), the influence of the potential scan rate during cyclic voltammetric measurements of the ratio between reversible and irreversible processes was found to be of a complicated nature. The effect of scan rate on the voltammogram may confirm the irreversible behavior. While in a Nernstian (reversible) system, the peak potential is scan rate independent, in irreversible systems it does depend on the scan rate.

The anodic current onset may be associated with the decomposition of the polymer electrolyte. Figure 5 shows good stability until 5.0 V (versus Li/Li⁺) for Agar _{32.30%}Mg(CF₃SO₃)₂, followed by an oxidation. Increase of potential sweeping rate increases the cathodic peak current, and shifts the cathodic peak potential in negative direction.

When we make the electrochemical stability measurement at 80°C , at which Agar-Mg triflate electrolyte displays good conductivity for practical applications, and presents a

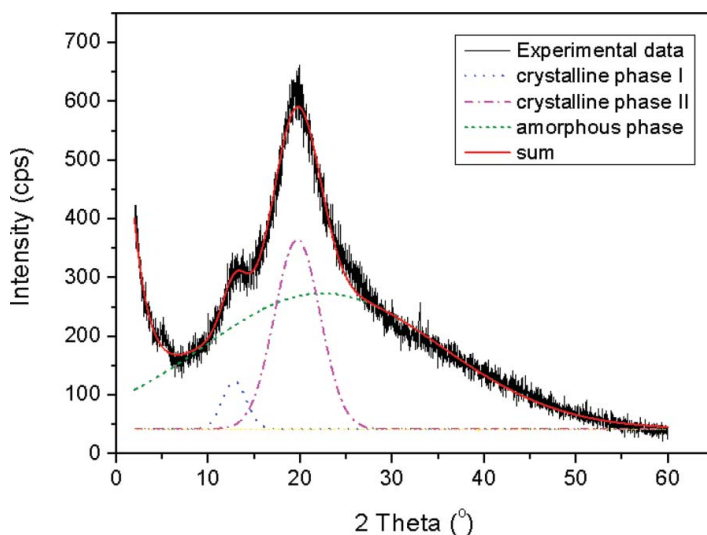


Figure 6. X-ray diffraction of electrolyte Agar_{16.79%}Mg(CF₃SO₃)₂.

stability potential not lower than 3.5 V (versus Li/Li⁺). This value is lower than stability measurement at 25°, but is a value considered adequate for commercial applications.

Figure 6 the typical X-ray diffraction (XRD) patterns obtained for the Agar_{16.79%}Mg(CF₃SO₃)₂-based electrolyte measured at room temperature. The diffractogram of agar powder (not showed here) revealed an ordered structure by presence of very accentuated

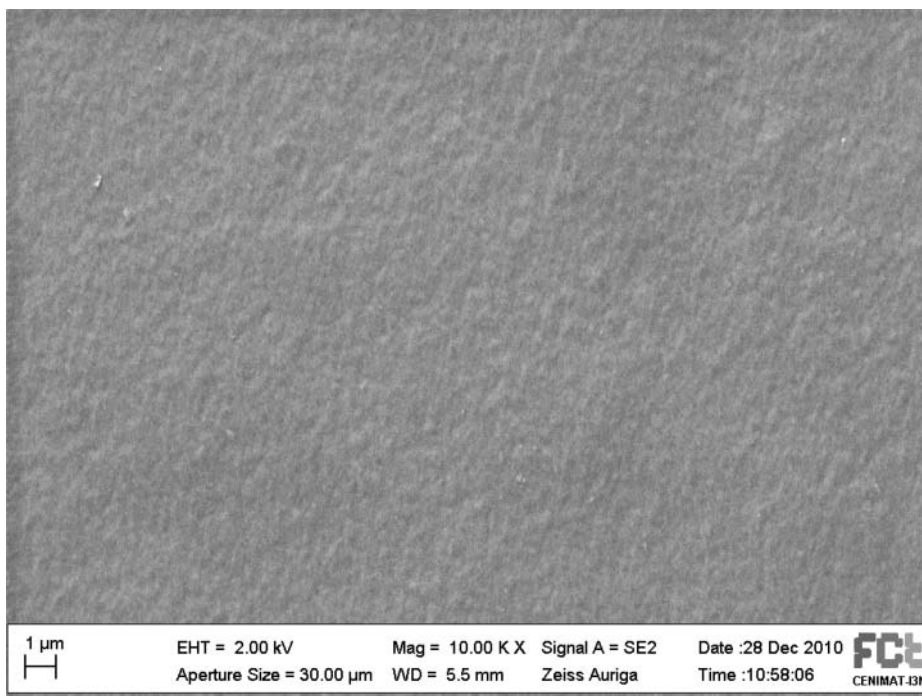


Figure 7. SEM picture of the Agar_{16.79%}Mg(CF₃SO₃)₂.

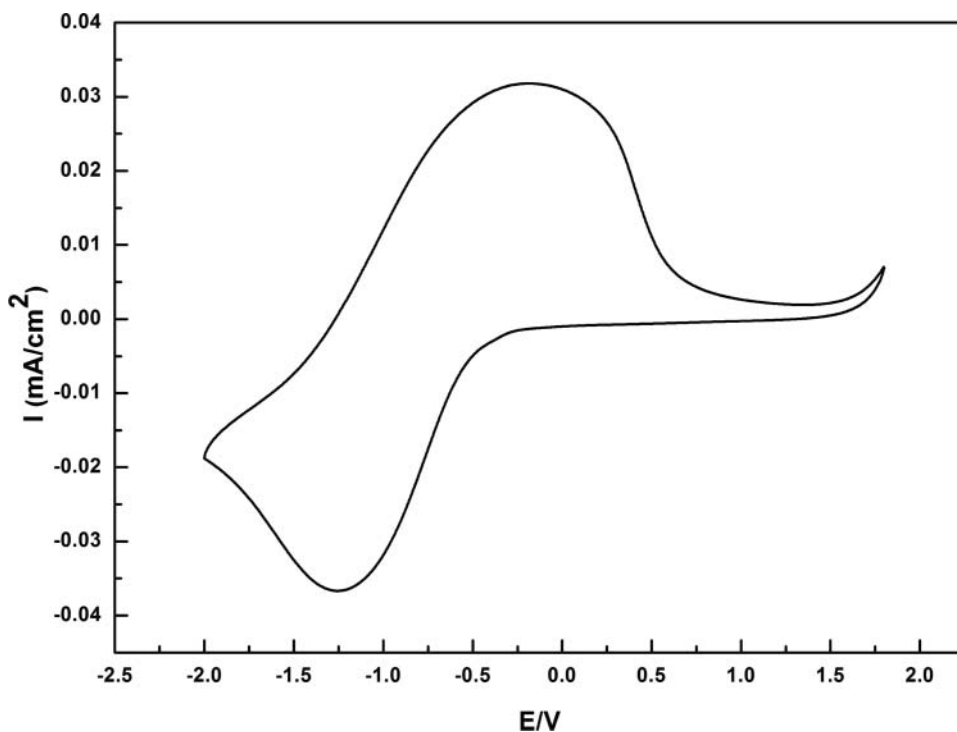


Figure 8. Cyclic voltammetry of electrochromic window with WO₃/agar–magnesium triflate-based electrolyte/CeO₂–TiO₂ configuration.

peak at $18.6^\circ 2\theta$ and a slight shoulder at $14.3^\circ 2\theta$, similarly to the results of 19.9° and 13.83° , respectively, reported for pristine agar films [23]. The addition of magnesium triflate to the sample composition promotes a change of the structural arrange of the polymer chains, evidencing the displacement of the peaks to 19.4° and $12.2^\circ 2\theta$. The deconvolution of the diffraction profile in different Gaussian lines (Fig. 6) reveals very broad components of the fully disordered part in the sample and three narrower bands attributed to the ordered regions. From the deconvoluted plot, the degree of crystallinity of this sample is found to be about 20%. Moreover, as the homogeneity without any phase separation and good surface uniformity of agar-based electrolyte with magnesium triflate samples observed in the SEM pictures (Fig. 7) is observed, the increase of the intensity at low angles can be due to salt aggregates dispersed in the amorphous structure.

To verify a performance of the agar–magnesium triflate ionic conducting membranes, small electrochromic devices with glass/ITO/WO₃/agar–magnesium triflate electrolyte/CeO₂–TiO₂/ITO/glass configuration were assembled. Typical cyclic voltammogram of an electrochromic device (ECD) with WO₃/agar–magnesium triflate/CeO₂–TiO₂ configuration measured during the second chronoamperometric cycles is shown in Fig. 8. One cathodic peak centered at -1.25 V is observed and is associated to the color process due to the reduction of WO₃ coating. The anodic peak (bleaching) shape changes as voltammetric cycling is centered at 0 V and is related to oxidation process.

The charge density response measured by chronoamperometry (-2.5 V/ $+2.0$ V; 15 s/15 s) of ECD containing solid electrolyte based on agar and Mg(CF₃SO₃)₂ is shown in Fig. 9. From these measurements, it can be stated that the insertion (coloration) is fast.

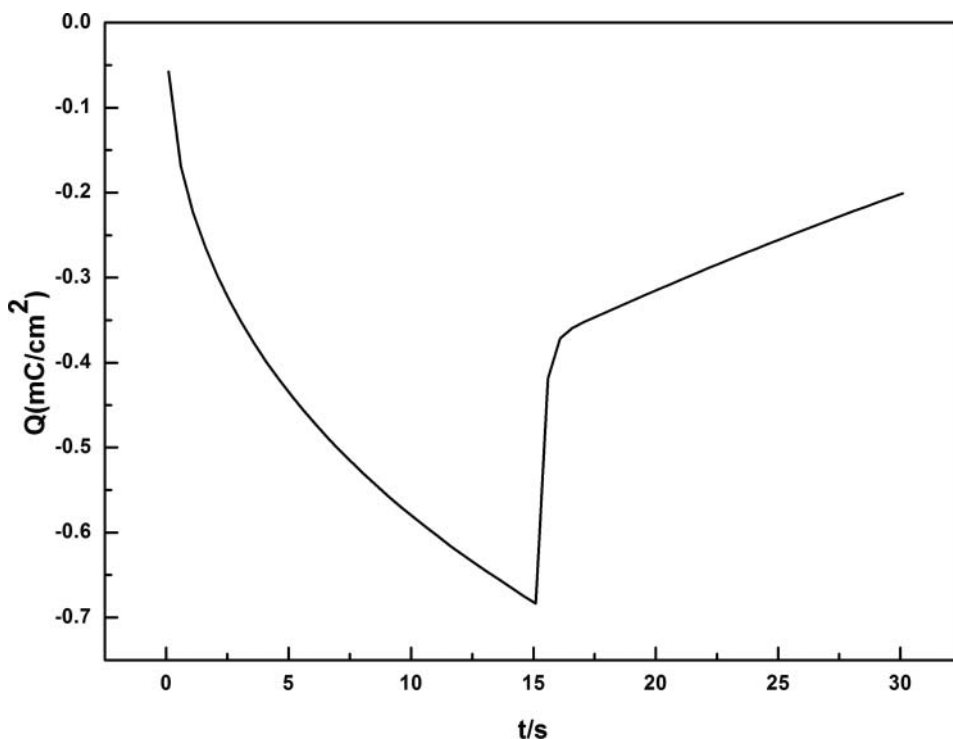


Figure 9. Charge densities for ECDs with electrolytes based on agar and $\text{Mg}(\text{CF}_3\text{SO}_3)_2$.

For instance, for the second cycle, the inserted charge at -2.5 V reaches -0.7 mC/cm^2 in 15s. The charge extraction occurs faster and the ECD is already discolored after applying $+2.0$ V potential during 2s. This extraction is also faster than that obtained with ECDs containing starch-based electrolytes [24], gelatin-based electrolytes [25], and comparable to the ECD with agar-based electrolyte [26]. Also, whenever the devices become transparent, the extracted charge during the first cycles is slightly smaller than the inserted one.

3. Conclusion

The Mg^{2+} -doped biohybrids based on agar host matrix have been synthesized by the solvent casting method. In practical, all solid-state electrochemical devices, although the magnitude of ionic conductivity is undoubtedly of prime importance, other aspects, such as, the thermal, mechanical, and electrochemical stabilities are essential. Thus, in spite of the modest ionic conductivity displayed by the optimal biohybrid material, its high thermal stability and good mechanical properties encourage further investment in this system, which has lower environmental impact than conventional electrolytes used at present in commercial devices. It is clear that the performance of the ECD reported in those works needs to be investigated in more depth. For instance, long-term durability tests under a wide range of conditions must be demonstrated if architectural window applications are envisaged.

Acknowledgments

The authors are pleased to acknowledge the financial support provided by the University of Minho and the Fundação para a Ciência e Tecnologia (contracts project no. F-COMP-01–0124-FEDER-022716 (ref FCT PEst-C/QUI/UI0686/2011) FEDER-COMPETE, FCT-Portugal; ELECTRA – PTDC/CTM/099124/2008) for laboratory equipment and research staff and financial support given by the Brazilian agency CNPq.

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