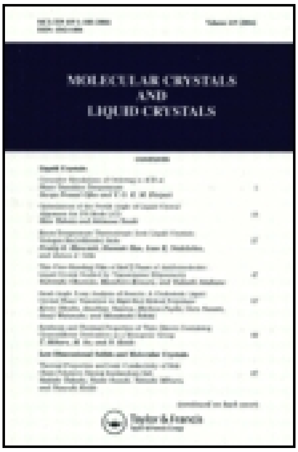

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Agar-Based Gel Electrolyte for Electrochromic Device Application

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Agar-Based Gel Electrolyte for Electrochromic Device Application

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Gel Polymer Electrolytes (GPE) based on agar and containing $LiClO_4$ have been prepared, characterized and applied to electrochromic devices. The ionic conductivity revealed the best result of 6.5×10^{-5} S/cm for the sample with 17 wt.% of $LiClO_4$, which increased to 5.4×10^{-4} S/cm at 72°C. The GPE have been used in electrochromic devices (ECD) with K-glass/WO_3/GPE/CeO_2-TiO_2/K-glass configuration. The ECD changed transmittance values up to 30% between the colored and transparent states. The charge density measurements revealed an increase of 5.5 to 7.5 mC/cm^2 from the first to 500th cycles and then a decrease to 4.4 mC/cm^2 during the next 4500 cycles. Coloration efficiency (η) of 25 cm^2/C was obtained.

Keywords Agar; electrochromic devices; gel polymer electrolyte; ionic conductivity

Introduction

The production, storage and distribution of energy are imperious necessities of industries and modern society in general. Moreover, fields, such as aerospace, electronic circuitry, or the need for new architectures for computers have required more and more devices as solid-state batteries, sensors and portable electrochemical devices. In such a context the development of solid state electrolytes has been a central challenge faced by the scientific research [1,2] and the best candidates for such applications have been ceramics, polymers and hybrid materials [3].

A solid polymer electrolyte (SPE) consists of a salt dissolved in a polymer matrix forming an ion conducting solid solution. Over the past last two decades different systems have been extensively studied, most of them based on poly(ethylene oxide) [3]. More recently electrolytes based on natural polymers, such as hydroxyethyl cellulose [4], starch [5], chitosan [6–8] and gelatin [9] have been alternatively proposed. In the case of gelatin- and chitosan-based systems, a high protonic conductivity has also been demonstrated [6,10].

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The ionic conductivity in solid polymer electrolytes is due to the segmental motion of the polymeric chains, which continuously create free volume for ions migration. On the other hand, in such systems, the population of ions and electrons must be large in order to avoid problems with migration and ohmic resistance. Most of the investigated SPEs based on poly(ethylene oxide) use Li^+ as conducting species [11,12], but proton conductive systems have also been investigated [13].

An important approach to increase the ionic conductivity of polymer electrolytes is the so-called plasticization process, to which small organic molecules, such as ethylene carbonate, poly(ethylene glycol) (PEG), glycerol, etc. are added. These plasticizers improve the ionic conductivity by (i) increasing the amorphous phase content, (ii) dissociating ion aggregates and (iii) lowering the glass transition temperature (Tg) of the system [14]. To achieve these improvements plasticizers should have high dielectric constant and low vapour pressure [15,16]. Among these systems gel electrolytes based on agar with acetic acid have been reported [17].

The present paper reports on the obtaining and characterization of agar-based gel electrolytes. Agar, similarly to starch, is a heterogeneous mixture of two polysaccharides: agaropectin and agarose. Although both polymers share the same galactose-based backbone, agaropectin presents acidic side-groups, such as sulfate and pyruvate, while agarose has a neutral charge. The surface morphology of the films was characterized by Scanning Electronic Microscopy (SEM), the structure of the films was examined by X-ray diffraction measurements, and the transmittance of the films was measured by UV-Vis spectroscopy. The influence of lithium salt concentration on the ionic conductivity values was obtained by impedance spectroscopy.

The agar-based electrolytes obtained in the form of transparent membranes were then used to make small electrochromic devices with K-glass/WO_3/agar-based electrolyte/CeO_2-TiO_2/K-glass configuration. These devices were characterized by UV-Vis spectroscopy and electrochromic efficiency.

Experimental

In order to prepare the electrolytes, 0.5 g of agar (Aldrich®) were dispersed in 30 mL of milli-Q water and heated under magnetic stirring for a few minutes up to 100°C to complete the dissolution. Next, 0.5 g of glycerol as a plasticizer, 0.5 g of formaldehyde and different quantities of lithium perchlorate (0.05 to 0.7g, 3 to 32 wt.%) were added to this solution under stirring. The resulting viscous solution was then cooled down to 30°C, poured in Petri dishes and let to dry up for 48 h at 40°C. The resulting transparent free-standing membranes with 0.12 mm thickness were stored in a dry box.

Stable coatings sols for WO_3 were prepared according to Schmidt et al. [18]. They employ a modified synthesis, based on the reaction of tungsten metal powder with an excess of hydrogen peroxide solution (30% solution) in the presence of ethanol and glacial acetic acid to yield the peroxotungstic acid. The reaction was conducted with appropriate cooling to keep the temperature at 0°C. The clear yellow sol formed was then dried and the powder redispersed up to 25 wt.% in ethanol as required. The coating sol produced could be stored for several weeks at 6°C without any detrimental effect on the coating properties [19]. K-glasses were coated by dip-coating (withdrawal rate of 4 mm/s) under controlled temperature (20°C) and humidity (RH = ∼30–40%). The coated substrates then underwent the heat treatment for 1 h at 240°C. Thin crack-free films with thicknesses of about 200 nm were prepared in a single dip-coating step with an excellent optical quality.

The CeO_2-TiO_2 was prepared by dissolving $Ce(NO_3)_3 6H_2O$ (0.056 mol) and $Ti(O^iPr)_4$ (0.069 mol) in 250 mL of ethanol followed by stirring the sol at 30°C for 4 days [20]. The

CeO_2-TiO_2 layers were deposited on K-glass substrate by the dip-coating technique with a withdrawing rate of 4 mm/s at 20°C with 38% air humidity. The layers were then heated in air from room temperature to up to 550°C with a heating rate of 2.5 K/min, kept at 550°C for 1 h, and then cooled down to room temperature in an oven for about 5 h.

Electrochromic devices with glass/FTO/WO_3/agar electrolyte/CeO_2–TiO_2/FTO/glass configuration and size of 7×4 cm^2 were obtained by assembling the two pieces of coated glasses. A 1-mm-thick and 5-mm-large spacer (3M tape Scotch) was glued on the four edges of 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 viscous agar-based electrolyte was injected with a syringe into the mounted cells, which were finally sealed with protective tape.

Impedance spectroscopy measurements were used to determine the frequency dependence of the electrolyte ionic conductivity. 1.54 cm^2 round pieces of the electrolyte were pressed between two steel electrodes. The system was installed in a teflon® cell under vacuum. The measurements were taken with Solartron equipment model 1260, by applying a voltage of 5 mV rms amplitude and varying the frequency in the 10^1 Hz–10^7 Hz range.

The structure of the films was examined by X-ray diffraction measurements using Siemens D-5000 instrument with CuK_α radiation ($\lambda = 1.5418$ Å).

The UV-Vis optical spectra were recorded with a Cary 5E Varian spectrophotometer between 200 to 1000 nm for polymer electrolyte and 300 to 2500 nm for electrochromic device, respectively.

The SEM micrographs were obtained with a LEO model 440 scanning microscope.

Results and Discussion

The ionic conductivity (σ) of the agar-based electrolytes at room temperature is presented as a function of the $LiClO_4$ salt amount in Fig. 1. The ionic conductivity (σ) increases in

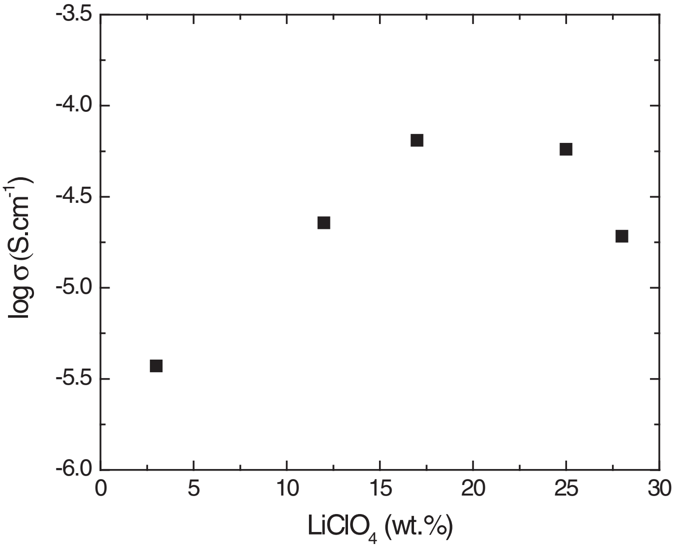


Figure 1. Effect of the lithium salt content on the ionic conductivity of the electrolyte measured at room temperature.

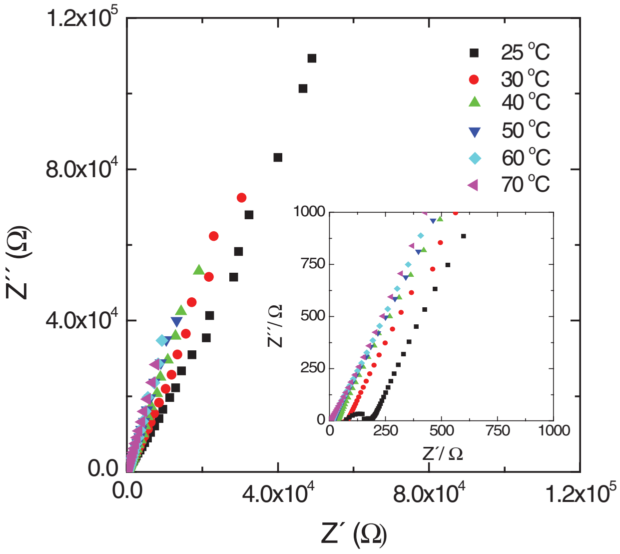


Figure 2. Complex impedance plots for the agar electrolyte containing 17 wt.% of $LiClO_4$ at different temperatures.

function of the amount of $LiClO_4$ to reach a maximum of 6.5×10^{-5} S/cm for 17 wt.% of $LiClO_4$. This is certainly related to the increase in the number of mobile charge carriers. However a decrease in the ionic conductivity is observed for higher amounts of $LiClO_4$ salt in the electrolyte, probably due to the formation of aggregates as already observed for agar-based electrolytes [17].

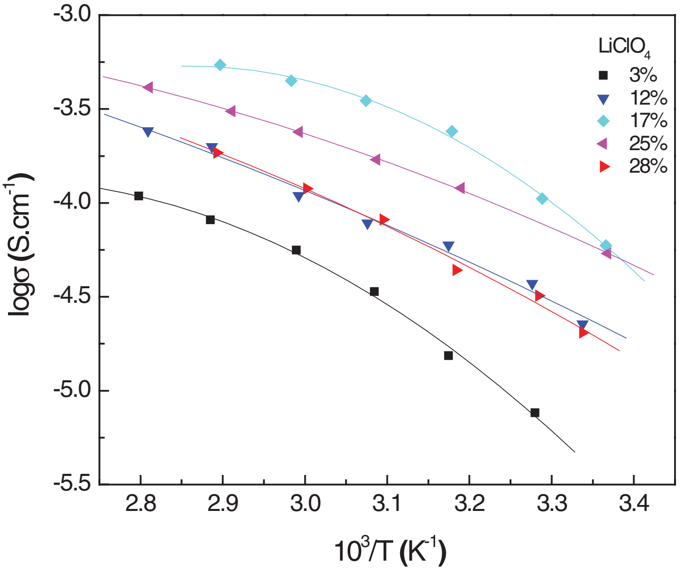


Figure 3. Temperature dependence conductivity of the agar-based electrolyte as a function of $LiClO_4$ content.

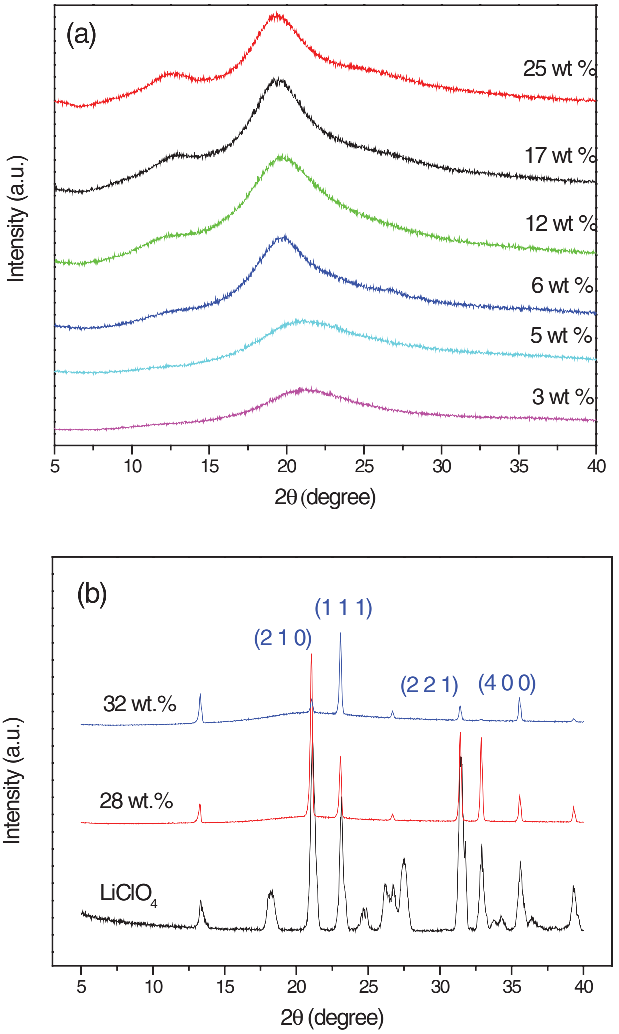


Figure 4. X-ray diffraction profiles of agar-based electrolytes with different $LiClO_4$ contents: (a) 3 to 25 wt.% and (b) 28 and 32 wt.%.

Figure 2 shows a typical impedance plots of the agar-based electrolyte prepared with the optimum concentration of $LiClO_4$ salt (17 wt.%) and measured at various temperatures. The values of the bulk resistance R_b decrease with the increase in the temperature, as better shown in the inset of Fig. 2, indicating an increase in the Li^+ ions mobility [21]. The intercept of the semicircle with the real axis gives the electrolyte bulk resistance (R_b). The ionic conductivity is then deduced from the R_b values by employing the formula $\sigma = l/R_bA$, where l is the thickness of the electrolyte sample and A is the contact area. The ionic conductivity is found to increase one order of magnitude when the temperature is varied from room temperature to 72°C, respectively and the films are found to be mechanically stable. At higher temperatures, thermal movement of polymer chain segments and the dissociation of the lithium salt are improved, inducing an increase in total ionic conductivity. In fact, an incomplete semicircle is observed as increasing the temperature (Fig. 2 inset), that suggests the appearance of a capacitive component at high frequencies.

The evolution of the ionic conductivity as a function of temperature in the range of 298 to 353 K for the samples with different salt concentrations is shown in Fig. 3. For the electrolyte with 17 wt.% it is possible to observe that the value increases from 6.5×10^{-5} S/cm at 25°C to 5.4×10^{-4} S/cm at 72°C. This increase is interpreted as a complex behavior of a hopping mechanism between coordinating sites, local structural relaxations and segmental motions of the polymer salt complexes. As the temperature increases, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion [22].

These results follow a Vogel-Tamman-Fulcher (VTF) thermally activated process model expressed by $\sigma = (A/T^{1/2}) \exp[-B/k(T-To)]$, where k is the Boltzmann constant, T is the temperature and B is the pseudo activation energy. The pseudo activation energy value of 11 kJ/mol is similar to those obtained for polymer electrolytes based on agar with acetic acid [17] or other natural macromolecules [23,24].

Figure 4 shows a typical X-ray diffraction pattern obtained for the agar-based electrolyte with different salt concentrations measured at room temperature. The samples with low salt amounts (3 and 5 wt.%) reveal broad diffuse bands centered at approximately $2\theta = 21°$. For lithium comprised between 6 and 25 wt.% it is possible to observe a displacement of this band to $2\theta = 19°$ and the appearance of a new small shoulder at $2\theta = 12°$, as already noted in agar-acetic acid-based membranes [17]. At high $LiClO_4$ amount (28 and 32 wt.%, Fig. 4b) clear crystalline peaks attributed to $LiClO_4$ can be observed. The presence of theses peaks and consequently salt crystallization explain the decrease in the ionic conductivity values, as shown in Fig. 1.

Figure 5 shows the optical transmittance of a 0.12 mm thick layer of the electrolyte containing 17 wt.% of $LiClO_4$ as well as almost zero transmission intensity below 230 nm, which starts to increase to reach 87% at 550 nm. After that the transmission is practically constant, indicating that the agar-based ionic conducting membranes will be optically well

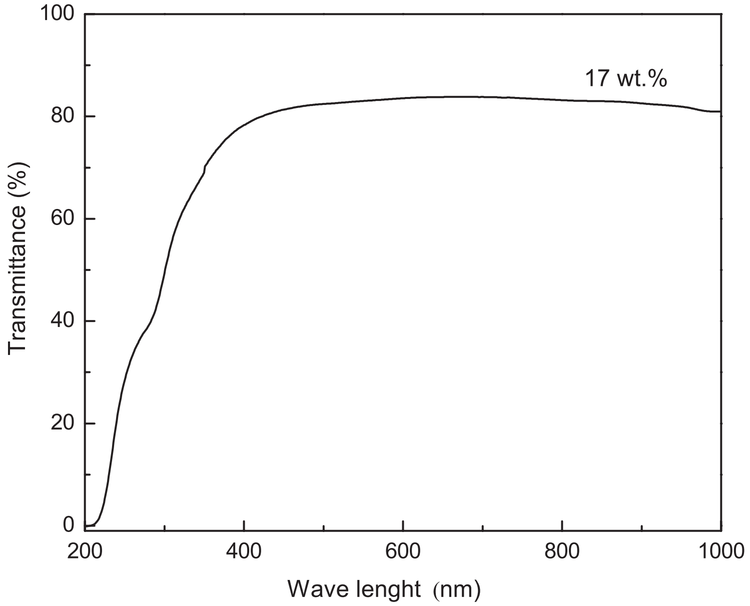
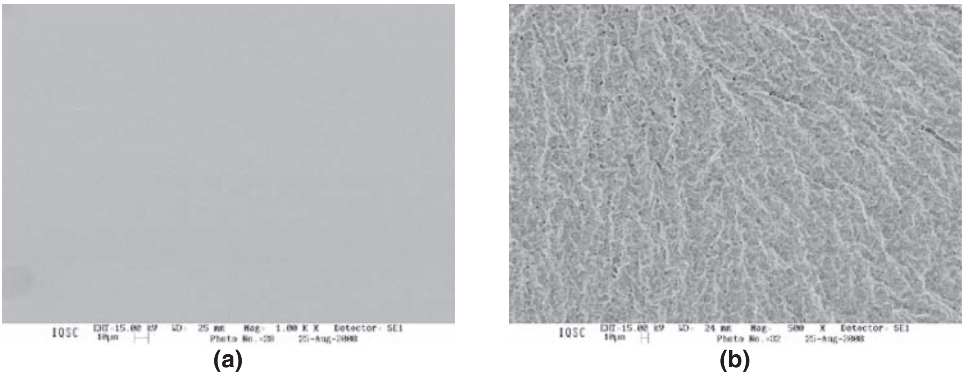


Figure 5. Optical transmittance measurement of agar-based electrolyte with 17 wt.% of $LiClO_4$ contents.



(a)

(b)

Figure 6. SEM micrographs of agar-based electrolytes with 28 wt.% (a) and 32 wt.% (b) of $LiClO_4$.

adapted to be applied to electrochromic devices. Similar results were obtained for the ionic conducting agar-based samples with different acetic acid concentrations [17].

Scanning electron micrographs (SEM) of the agar-based electrolytes with different amounts of $LiClO_4$ are presented in Fig. 6. A comparison of the surface morphology shows no difference in the surface properties and texture of these samples until 28 wt.% of lithium content (Fig. 6a). The SEM micrographs of the sample with 32 wt.% of the lithium salt (Fig. 6b) reveal a different morphology probably due to the salt crystallization, as observed in Fig. 4.

The UV–vis transmission spectra of the electrochromic device in the range from 300 to 2500 nm for the 500th cycle are shown in Fig. 7. A transmittance variation of 24% between

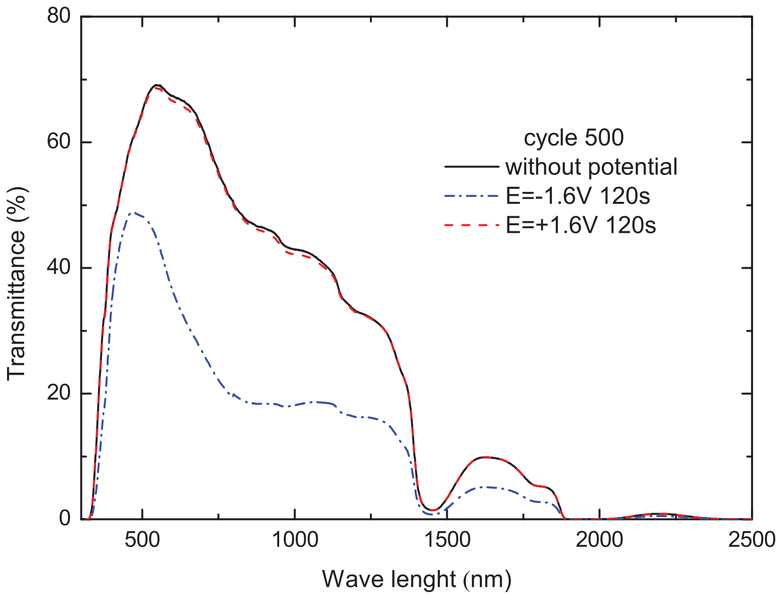


Figure 7. Transmittance spectra for ECD composed of WO_3/agar-based electrolye/CeO_2-TiO_2 measured during 500th cycle. The ECD was polarized for 120s at −1.6 V for colored state and 120s at +1.6 V for bleached state.

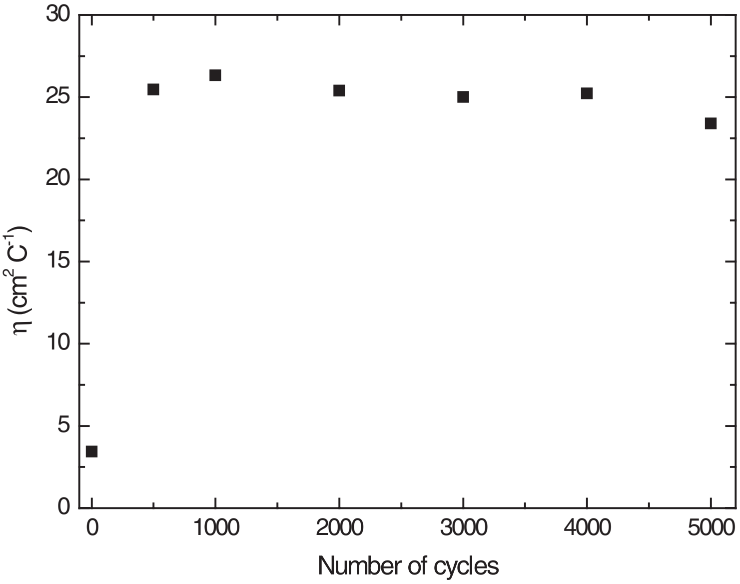


Figure 8. Electrochromic efficiency for ECD composed of WO_3/agar/CeO_2-TiO_2 measured during 5000 cycles.

the bleached (68% of transmittance) and colored states (44% of transmittance) occurs in the visible range of the spectra with a maximum at 550 nm. At 800 nm this difference is approximately 30% and the transmittance values drop down from 49% (bleached state) to 19% (colored state). The difference between the colored and bleached states decreases; at $\lambda > 1400$ nm it is lower than 10% and for $\lambda > 1800$ nm it becomes practically zero. These results are comparable to those obtained with electrochromic devices built with Nb_2O_5:Mo electrochromic coating and gelatin-based electrolytes with lithium salt [25], and to electrochromic devices built with other polymeric electrolytes reported by Heusing and Aegerter [26].

The colouration efficiency (η) at 550 nm is depicted in Fig. 8. The values increase rapidly from approximately 3 cm^2/C (1st cycle) to 25 cm^2/C (500th cycles) and remain practically stable until 4000th cycle. After that the values decrease to 23 cm^2/C for 5000 chronoamperometric cycles.

Conclusions

Polymer gel electrolytes based on agar and containing $LiClO_4$ salt were prepared and characterized by impedance spectroscopy. The obtained results revealed that the lithium salt concentration influences the ionic conductivity of electrolytes and the best values of 6.5×10^{-5} S/cm at room temperature were obtained for 17 wt.% of $LiClO_4$. It was also stated that the increase in temperature up to 72°C promotes an increase in the ionic conductivity to 5.4×10^{-4} S/cm. These results show a VTF behavior with an activation energy of $E\text{a} = 11$ kJ/mol. The samples in the self-standing membranes form with low salt concentration were predominantly amorphous, showing a transparency of 90% in the visible range of the electromagnetic spectrum and a microscopically uniform surface. 7cm×4cm electrochromic devices with WO_3/agar–$LiClO_4$/CeO_2–TiO_2 configuration were prepared.

These devices showed a transmittance change of 24% between the colored and transparent states measured at 550 nm and 30% at 800 nm. A coloration efficiency (η) of 25 cm^2/C was obtained during 5000 chronoamperometric cycles.

Acknowledgments

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