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Magnetic resonance and conductivity study of gelatin-based proton conductor polymer electrolytes

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ABSTRACT

This work report results from proton nuclear magnetic resonance (NMR), continuous-wave (CW-EPR) and pulsed electron paramagnetic resonance (P-EPR) and complex impedance spectroscopy of gelatin-based polymer gel electrolytes containing acetic acid, cross-linked with formaldehyde and plasticized with glycerol. Ionic conductivity of 2×10^{-5} S/cm was obtained at room temperature for samples prepared with 33 wt% of acetic acid. Proton (^{1}H) line shapes and spin-lattice relaxation times were measured as a function of temperature. The NMR results show that the proton mobility is dependent on acetic acid content in the plasticized polymer gel electrolytes. The CW-EPR spectra, which were carried out in samples doped with copper perchlorate, indicate the presence of the paramagnetic Cu^{2+} ions in axially distorted sites. The P-EPR technique, known as electron spin echo envelope modulation (ESEEM), was employed to show the involvement of both, hydrogen and nitrogen atoms, in the copper complexation of the gel electrolyte.

1. Introduction

Over the last decades, there has been growing interest in solid polymer electrolytes (SPE) because of their potential application in electrochemical devices [1–3]. Among these materials, polymer-based proton conductors have received considerable attention due to its application in fuel cells, humidity sensors and electrochromic devices [4–6]. A number of studies have addressed the complexes formed by a polymer such as poly(ethylene oxide) or poly(vinyl alcohol) (PVA) and strong acids like H_3PO_4, H_2SO_4 or HCl [2,7–10]. In other respects, polymer electrolytes obtained from natural polymers – as chitosan, starch and cellulose derivatives – have been drawing attention because of its specific properties, such as biodegrability, low production cost and good physical and chemical properties [11–19].

In the last decades, the ionic dynamics of proton conducting polymer gel electrolytes have been extensively studied. Przytuski et al. reported conductivity, DSC and infrared spectroscopy measurements in poly(acryl amide) hydrogels doped with H_3PO_4 and H_2SO_4 and discussed the influence of the acid and water concentration on the proton transport mechanisms [20,21]. Grotthus or vehicle-type proton transportation mechanisms were postulated depending on the acid used on the hydrogel. Wieczorek et al. reviewed the studies on nonaqueous conducting gel electrolytes and discussed the effect of the solvent on the physical–chemical properties of the gel electrolyte [22]. In this case, a Grotthus or a vehicle mechanisms was postulated depending with the use of protophilic or protophobic solvent on the gel electrolyte. Chung et al. examined the mobility of the phosphorus species on the proton conducting gel electrolytes based on methyl methacrylate and glycidyl methacrylate polymer matrices containing perdeuterated H_3PO_4 plasticized with propylene carbonate, dimethylacetamide and dimethyl formamide (DMF) by ^{31}P pulsed field gradient PFG-NMR [23]. Jeffrey et al. reported electrical conductivity, viscosity, ^{2}H and ^{31}P PFG NMR measurements on the gel electrolyte formed by deuterated phosphoric acid dissolved in DMF and poly(glycidyl methacrylate) (PGMA) [6]. Qiao et al. reported conductivity, FTIR and DSC for the non-aqueous gel electrolyte formed by poly(ethylene oxide) modified poly(methacrylate) (PEO-PMA) plasticized by poly(ethylene glycol) – dimethyl ether (PEGDE) and containing H_3PO_4 [24]. The authors identified protonic interactions between the acid and the PEO-PMA matrix and entrapped plasticizers in the gel. Morita et al. reported conductivity measurements and examined capacitance behavior of the non-aqueous gel electrolyte formed by poly(vinylidene difluoride-co-hexafluoropropylene) (PVdF-HFP) swollen with DMF solutions containing phosphoric acid or trifluoro methanesulfonic acid [25].

Recently it was proposed a new ionic conducting system based on commercial gelatin. This polymer gel electrolyte showed conductivity of the order of 5×10^{-5} S/cm at room temperature, good electrochemical reversibility and very high transparency [17,26,27]. In the present work we report conductivity and proton (^{1}H) NMR

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Table 1
Sample compositions (in wt%).

	Gelatin	Glycerol	Acetic acid	Formaldehyde
Sample 1	47	29	18	6
Sample 2	42	27	26	5
Sample 3	38	24	33	5

line shapes and spin-lattice relaxation measurements as a function of temperature in a series of conducting gel electrolytes based on a gelatin network containing acetic acid (CH_3COOH) plasticized with glycerol and cross-linked with formaldehyde. NMR is a powerful tool used in the study of ionic and polymer dynamics in polymer electrolytes [28–32]. In order to investigate the coordination environment of the cation in this type of gel electrolyte we also undertake a continuous-wave and pulsed electron paramagnetic resonance (CW-EPR and P-EPR, respectively) investigation on samples slightingly doped with copper perchlorate. EPR is a well-known sensitive spectroscopic technique for the study of the location, nature and electronic properties of Cu^{2+} centers. The Cu^{2+} ion was found to be a particularly useful probe since its EPR spectra are readily observable over a large temperature range [33–36].

2. Experimental

The electrolytes were prepared according to the following description. Commercial uncolored gelatin (Oetker®) was dispersed in 15 mL of water and heated under magnetic stirring up to 50 °C for complete dissolution. Glycerol as plasticizer, formaldehyde as cross-linking agent and acetic acid were added to the solution under stirring. This viscous solution was then cooled down to room temperature and poured on Petri plates. The transparent films obtained were dried in a dry box for three days. Table 1 list the composition of the three samples investigated. The ionic conductivities were obtained by measurements of the complex impedance in a Solartron model 1260 using an ac potential of 50 mV, for temperature and frequency ranging between 25 °C to 85 °C and 10 Hz to 1 MHz, respectively. Proton (^1H) NMR linewidth and spin-lattice relaxation measurements were carried out in the membrane samples from 150 K to 330 K using a home-built pulsed NMR spectrometer equipped with a TECMAG NMR kit, operating at 36 MHz. Nuclear spin-lattice relaxation times were determined using the standard saturation-recovery method, being the magnetization recoveries toward equilibrium found to be exponential throughout the entire temperature range. Continuous-wave electron paramagnetic resonance (CW-EPR) and electron spin echo envelope modulation (ESEEM) spectra were obtained at 30 K on a Bruker Elexsys E580 spectrometer operating at 9.5 GHz.

3. Results and discussion

3.1. Conductivity

Fig. 1 shows the Arrhenius plot of the ionic conductivity of the three gel samples investigated. The ionic conductivity at 300 K of the samples are 2.5×10^{-6} S/cm (sample 1), 2×10^{-5} S/cm (sample 3) and 4×10^{-5} S/cm (sample 2). The activation energy obtained from the fitting of the experimental data are 47.3 ± 3.5 kJ/mol (sample 1), 35.3 ± 1.8 kJ/mol (sample 3) and 29.5 ± 1.8 kJ/mol (sample 2).

3.2. Nuclear Magnetic Resonance

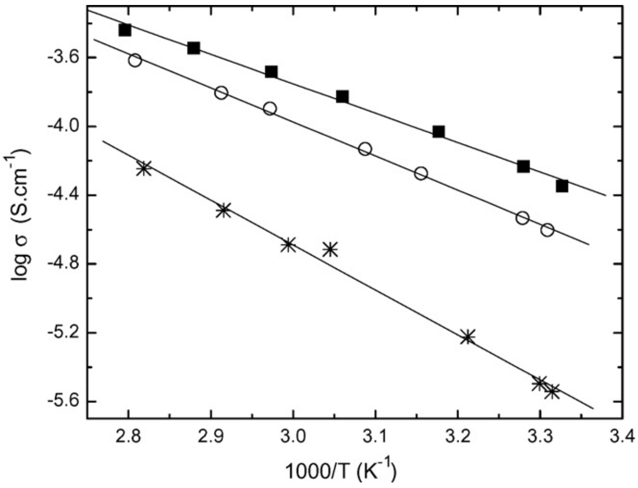

Fig. 1. Arrhenius plot of ionic conductivity of the gel electrolytes containing 18 wt% (*), 33 wt% (○) and 26 wt% (■) of acetic acid.

The low temperature (180 K) ^1H NMR line shape consists of a narrow peak flanked by a pair of broader lines separated by ≈10 G. Such kind of spectrum has been observed previously in polymer gel electrolytes formed by hydroxyethylcellulose plasticized with glycerol and containing lithium perchlorate [45]. The side peaks cab be attributed to a Pake doublet [37] assigned to paired protons in CH_2 and NH_2 groups of the gelatin, but may also have contribution from CH_3 groups of the glycerol, whereas the central line can be attributed to the superposition of ^1H signals belong to the OH and also CH_3 groups of the gelatin, glycerol and acetic acid. The inter-molecular interactions between molecular groups in the gel electrolytes are responsible for the broadening of the low temperature NMR spectrum. Above 220 K, the mobility of the protons in the gel electrolyte increases enough to average out the H–H magnetic dipole–dipole interactions producing a line narrowing. This effect has been documented widely in polymer electrolytes [38–40] and in proton conductors [41–43]. Fig. 2 shows the temperature dependence of the ^1H linewidth in the three gel electrolyte samples studied here. In polymer electrolytes, where the ion dynamics is coupled to the polymer segmental motions, there exists a well-established correspondence between the calorimetric glass transition temperature (T_g) and the onset of the motional line narrowing [32,38,39,44]. Therefore, one can estimate T_g^{NMR} of our gel electrolytes from the onset of the ^1H NMR line narrowing in Fig. 2. The line narrowing of the electrolyte with 26 wt% of acetic acid (sample 2) is near 215 K whereas those of the samples 1 and 3 are observed near 223 K (see Table 2). The

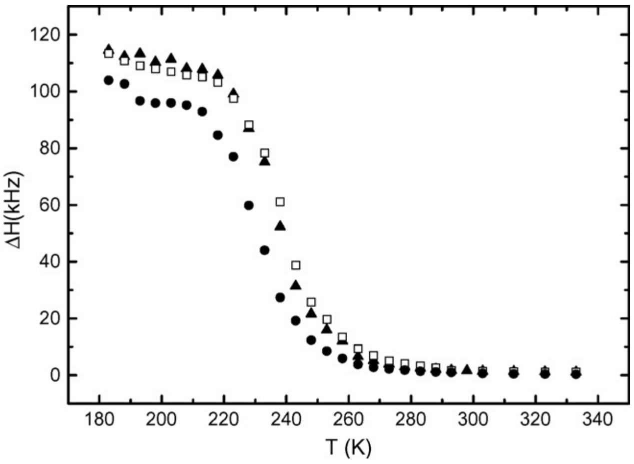

Fig. 2. Temperature dependence of the ^1H NMR linewidth in the gel electrolytes containing 18 wt% (▲), 26 wt% (●) and 33 wt% (□) of acetic acid, measured at the Larmor frequency of 36 MHz.