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NMR, conductivity and DSC study of Li^+ transport in ethylene glycol/citric acid polymer gel

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Abstract

In this present paper the influence of viscosity on the ionic dynamics of polymer gel electrolytes prepared by the Pechini polymeric precursor method is investigated by impedance spectroscopy, differential scanning calorimetric (DSC) and NMR techniques. Polymer gel electrolytes are formed by ethylene glycol (EG) and citric acid (CA) and lithium perchlorate. Room temperature conductivity of the order of 2.3×10^{-4} S/cm was obtained for the sample of EG/CA:$LiClO_4$ with lower viscosity ($\eta = 197$ cP). The results show that the ionic conductivity of the electrolytes increases for decreasing viscosity. Proton (^1H) and Lithium (^7Li) NMR lineshapes and spin–lattice relaxation times were measured as a function of temperature and viscosity (197–868 cP). The ^7Li relaxation process was found to be dominated by quadrupolar couplings. The activation energy extracted from the ^1H and ^7Li relaxation data (~0.23 eV) was found to be independent of the viscosity of the gel electrolyte. The ^7Li NMR relaxation results indicate an increase of the lithium ion mobility with decreasing viscosity.

Keywords: NMR; Ionic conductivity; Viscosity; Polymer gel electrolyte

1. Introduction

Solid polymer electrolytes (SPEs) have been the subject of substantial academic and technological interest, following the pioneering studies of Wright and Armand [1]. The polymer gel electrolytes have lately become of great interest on account of their use in secondary lithium batteries. The high ionic conductivity compared with the SPEs has made these materials promising for lithium battery applications [2–7].

Nuclear magnetic resonance spectroscopy (NMR) is a very powerful tool for studying ionic dynamics in solid polymer electrolytes. NMR lineshapes and spin–lattice relaxation times are measured as a function of temperature at the Larmor frequency $\omega_o = \gamma H_o$, where γ is the nuclear magnetogyric ratio and H_o is the external magnetic field. As an element-selective method, NMR studies can provide valuable information on the atomic and molecular motions that modulate the dipolar interactions and nuclear electric quadrupolar couplings [8–11].

In the last decades, a number of NMR studies have addressed the lithium dynamics of polymer gel electrolytes. Reiche et al., investigated the charge carrier transport of gel electrolytes based on oligo(ethylene glycol) O(EG) and $LiCF_3SO_3$ plasticized by dimethyl ether (DME) by ^1H, ^{19}F and ^7Li pulsed field gradient pfg-NMR technique. The results indicate a strong correlation between plasticized mobility and ion diffusivity [12–14]. Diffusion coefficients of Li^+ ions, anions and electrolyte solvent were also measured by the pfg-NMR technique in polymer gel electrolytes based on poly(vinylidene fluoride co-hexafluoropropylene) PVDF-co-HFP, containing nanoparticles and lithium triflate by Abbrent et al. Their results reflected the heterogeneous ionic environment in the nanocomposite mate-

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rials [11]. Saito et al., investigated the conduction mechanism of lithium polymer gel electrolytes based on PVDF-HFP and lithium salts by complex impedance and pfg-NMR techniques and discussed the results in terms of the interaction between the electrolyte and polymer chains, the carrier mobility and dissociation degree of the salt [3,15]. Hayamizu et al., reported several pfg-NMR studies of self-diffusion coefficient and conductivity of polymer gels composed of cross-linked PEO, γ-butyrolactone, propylene carbonate and lithium salts. The authors compared the individual diffusion coefficient with the conductivity of the electrolytes and asserted that the motion of the Li ions, although solvated by the GBL, is strongly associated with the polymer host [4,16,17]. Williamsom et al., measured the self-diffusion coefficient of polymer gel electrolytes based on PVDF and $LiCF_3SO_3$ with tetraglyme or dimethyl formamide DMF by ^{7}Li, ^{19}F and ^{1}H pfg-NMR technique and provided an estimation of the degree of ionic association as a function of temperature and salt concentration [18,19].

It has been recognized that the formation of a polyester between citric acid (CA) and ethylene glycol (EG) constitutes an important factor for the formation of resin intermediates in a Pechini type-process [20] to prepare stoichiometrically mixed oxide films and ceramic materials [21,22]. In this sense, the use of this polymer as an ionic conductor gel material is interesting due to its low cost, preparation easiness and also because it is possible to prepare samples with different chain lenght and cross-link degrees. Since the effects of preparation variables were found to be decisive factors on the properties of the resulting materials, it is important to study the influence of temperature and viscosity on the lithium mobility of the polymer electrolyte obtained from the polymerization of EG and CA with lithium salt. In a previous paper, we investigated the lithium ionic mobility of the polymer gel electrolyte formed by EG, CA and $LiClO_4$ by proton (^{1}H) and lithium (^{7}Li) NMR lineshape and relaxation. The ^{7}Li NMR results showed qualitative features associated with the lithium mobility in the polymer gel electrolyte, namely the presence of a line narrowing and a well defined ^{7}Li spin–lattice relaxation maximum [23]. In this present paper, the influence of viscosity on the ionic dynamics of these polymer gel electrolytes is further investigated by impedance spectroscopy and NMR techniques. Proton (^{1}H) and Lithium (^{7}Li) NMR lineshapes and spin–lattice relaxation times were measured as a function of temperature and viscosity in samples of EG/CA containing lithium perchlorate.

2. Experimental

The polymer gel electrolytes were prepared by means of the Pechini process [24]. The samples were obtained by dissolving ethylene glycol (EG) and citric acid (CA) (CA:EG = 1:4). The polymerization was performed at 110 °C for 0.5 h, 1 h, 2 h and 4 h to obtain different viscosity value, with $\eta = 197$ cP, 245 cP, 542 cP and 868 cP, respectively. Appropriate amount of polymer and salt $LiClO_4$ were weighed and dissolved to desired $LiClO_4$:CA ratio of 1:10. The viscosity experiment was performed using a torque viscosimeter Brookfield model DV-III. The DSC study was measured using Netzsch STA 409, with a heating rate of 20 °C/min, in a temperature ranging between −150 °C and 50 °C, under N_2 atmosphere. The ionic conductivity were obtained by measurements of complex impedance ac using a Solartron model 1260, in a temperature ranging between 10 °C and 80 °C, from 1 MHz to 10 Hz, using an ac potential of 50 mV. The ^{1}H spin–lattice relaxation times (T_1) measurements were carried out on a pulsed NMR spectrometer equipped with a TECMAG NMR-kit, operating at 36 MHz in the temperature range 180–360 K. The ^{7}Li NMR lineshapes and spin–lattice relaxation times (T_1) measurements were carried out on a Varian-400 MHz *Inova* NMR spectrometer operating at 155.4 MHz in temperature range of 180–360 K. Saturation–recovery pulse sequence ($\pi/2$ pulse $\approx 1.5\ \mu s$) was employed to determine spin–lattice relaxation times (T_1). ^{1}H and ^{7}Li magnetization recoveries toward equilibrium were found to be exponential throughout the entire temperature range.

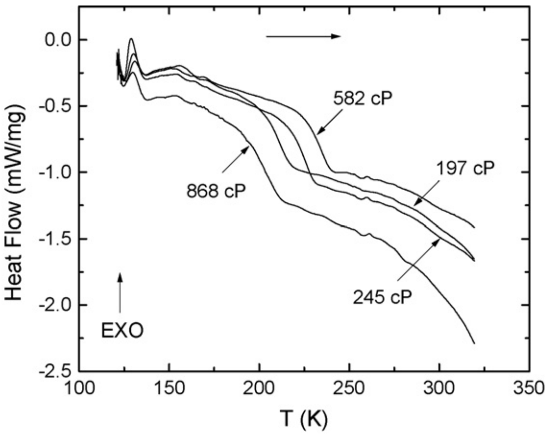

Fig. 1. DSC thermograms for EG/CA:$LiClO_4$ with different viscosities. The arrow on the figure indicates the scanning direction.

3. Results and discussion

Fig. 1 shows the DSC curve of EG/CA:$LiClO_4$ with different viscosity values. The sample with lower viscosity (197 cP) exhibited a glass transition at 202 K. With the increase of viscosity up to 582 cP, the glass transition shifted to a higher temperature at 226 K. These parameters can be observed in Table 1. However, the sample with the highest viscosity (868 cP) exhibited the glass transition at the lowest temperature (191 K). This is an unexpected behavior. A feasible explanation is a change in the polymerization mechanism during long reaction times, which could decrease the formation of intercrossing bonds. In this case, seeing that the chain length becomes higher, the probability of the intercrossing bond formation decreases, merely

Table 1
Polymerization times, viscosities (η) and glass transition (T_g)

Polymerization time (h)	η (cP)	T_g (K)
0.5	197	202
1.0	245	218
2.0	582	226
4.0	868	191