New Li^+ ion-conducting ormolytes

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Abstract

The preparation and characterization of two new families of lithium-conducting solid-state electrolytes is reported. Both systems are silica (SiO_2) – polyethyleneglycol (PEG_n) hybrid materials with (type I) or without (type II) covalent organic-inorganic chemical bonds. Their electrical conductivity has been studied by complex impedance spectroscopy between 20°C and 100°C in the frequency range 1 Hz to 10 MHz as a function of the polymer chain length ($200 < n < 1900$), polymer concentration and lithium concentration ($4 < [O]/[Li] < 80$). The highest room-temperature ionic conductivity ($\sigma \cong 6 \times 10^{-2}$ S cm^{-1}) has been found for type II material for ratios $[O]/[Li] = 15$ and $PEG_{300}/TEOS = 1.0$. The effect of the chain length on the polymer mobility has been studied by nuclear magnetic resonance by measuring the Li^+ line widths and the spin-lattice relaxation time T_1 between -100°C and + 100°C. The bonded chain mobility increases with the chain length (type II) while the opposite occurs with unbonded chain material (type I). Both types of materials present high ionic conductivity at room temperature and are adequate as Li^+-conducting electrolyte in all solid-state electrochemical devices.

Keywords: Sol–gel; Ormolyte; Li^+ conductivity; (NMR) nuclear magnetic resonance

1. Introduction

Many studies have been reported in the field of solid electrolytes [1] due to their potential for various applications such as batteries, energy and data storage, sensors, electrochromic and photochromic devices [2]. Systems showing conductivity induced by the addition of lithium offer the most favorable properties [3]. Recently, studies have been reported on hybrid materials obtained by reacting silicon alcoxydes with polyethers [4, 5]. They showed that poly(ethylene)oxide could act as a "solid" solvent for numerous chemical species, while the structural silica network reinforces mechanically the final material. Specific physical properties can be obtained by dissolving suitable doping agents within such network, e.g. lithium salt for ionic conductivity. The tailoring of the properties is strongly related to the connectivity of the two phases and the mobility of both the structural network and the active species.

This work reports on the preparation and structural properties of a new hybrid ionic conductor silica (SiO_2)-Polyethyleneglycol (PEG_n) with and without covalent organic–inorganic chemical bonds. The electrical properties of the materials and the mobility of the polymer chains and Li^+ ions have been determined by complex impedance spectroscopy and solid-state nuclear magnetic resonance (NMR) measurements.

2. Experimental

All chemical reagents are commercially available (Fluka, Aldrich). For the first family (type I) equimolar amounts of 3-isocyanatopropyltriethoxysilane (IsoTrEOS) and O,O′ Bis (2-aminopropyl)polyethyleneglycol (i.e NH_2–PEG–NH_2) were stirred together in tetrahydrofuran (THF) under reflux for 6 h. THF was evaporated and a pure hybrid precursor $_3(OEt)Si$–PEG–$Si(OEt)_3$ was obtained. 0.5 g of this precursor was mixed with 1 ml of ethanol containing amonium fluoride (NH_4F), with a ratio $NH_4F/Si = 0.005$ to which the desired quantities of the lithium salt ($LiClO_4$) were added. Finally 0.2 ml of water was added under stirring. A monolithic gel was obtained in 4 h. Ethanol was then slowly removed to give a piece of rubbery material. The existence of covalent chemical bonds between the silica network and the polymer chains has been reported [6, 7].

The materials of the second family (type II) were prepared by an ultrasonic method: 12.5 ml of tetraethoxysilane (TEOS) and 4 ml of water were stirred together under ultrasound to hydrolyze the TEOS. Then the desired quantities of (PEG_n, n = PEG molecular weight) were added in neutral pH conditions. The lithium salt ($LiClO_4$) was then introduced and dissolved under ultrasound in order to obtain a transparent monophasic liquid. Gelation occurred in a few minutes and the samples were allowed to dry slowly as a monolithic piece. Studies of similar samples prepared by the classic sol–gel method have shown that only weak physical bonds exist in these materials [4, 6].

The electrical properties of the samples were determined by complex impedance spectroscopy between 20°C and 100°C with a Solartron 1260 apparatus, in the range

1 Hz to 10 MHz, with an applied voltage amplitude of 5 mV. The samples were flat pieces of monolith about 0.5 mm thick. The contacts were obtained with elasticized conductive probes (Altoflex) pressed on the sample. Stable and reproductive values of the ionic conductivity were obtained by conditioning the dried samples under vacuum at 90°C for 24 h.

^{7}Li solid-state NMR spectra, consisting of only the central transition, were recorded between − 100° and 90°C at 32.9855 MHz using a TECMAG LIBRA system and a variable temperature double-resonance Doty probe. The line widths were measured from the Fourier transform of the free induction decays (FID) obtained by a simple 10 ms $\pi/2$ excitation. The ^{7}Li spin-lattice relaxation time T_1 was measured by the inversion–recovery method. When necessary, ^{1}H decoupling was used during the FID acquisition to improve the signal-to-noise ratio, allowing ^{7}Li T_1 measurements over a large temperature range. Full-widths at half-maxima (FWHM) were obtained by fitting the lineshape by Lorentzian or Gaussian functions, depending on the temperature ranges.

3. Results and discussion

3.1. *Type I materials with covalent bonds between the organic and inorganic network*

(a) *Effect of the lithium concentration*: Fig. 1 presents the variation of the room temperature conductivity σ_{amb} for the chemically bonded hybrids silica-PEG$_{200}$, silica-PEG$_{800}$ and silica-PEG$_{1900}$ as a function of the ratio [O]/[Li] (where the oxygens considered are only those of the ether type). The overall shape of the curves is similar and they present a maximum at the same value of the ratio [O]/[Li] $\cong$ 15, in contrast with the behavior observed in most polymeric systems in which σ_{max} occurs for [O]/[Li] = 8 [8, 9]. The values of the conductivity increase with the PEG$_n$ molecular weight and, for the data presented, the maximum ($\sigma = 1.2 \times 10^{-5}$ S cm^{-1}) is observed for $n = 1900$. Such materials are therefore quite adequate to be used in numerous applications.

For pure polymers [10], the increase of the conductivity with the salt concentration is attributed to long-range coulomb interactions. The decrease of σ at low [O]/[Li] ratio after the maximum is a consequence of the immobilization of the polymer chains by interactions with the Li$^+$ ions. In our materials, the saturation occurs at a lower concentration, showing that the PEG$_n$ chains mobility is smaller when both networks are chemically bonded. The temperature variation of the conductivity follows strictly an Arrhenius law $\sigma = \sigma_0 \exp(-E_a/RT)$. The variation of E_a with lithium concentration shows also a minimum for [O]/[Li] around 15.

(b) *Effect of the polymer chain length*: The ionic conductivity, σ_{amb}, increases when the polymer chain length increases (Fig. 1). It is well known that the conductivity of polymer electrolytes occurs via liquid-like motions of cations through the segmental motion of the neighboring polymer chains [1]. Therefore, the PEG chain mobility increases as the chain length increases. Judeinstein et al. [6, 7] have studied by electron paramagnetic resonance (EPR) the same samples without lithium and have

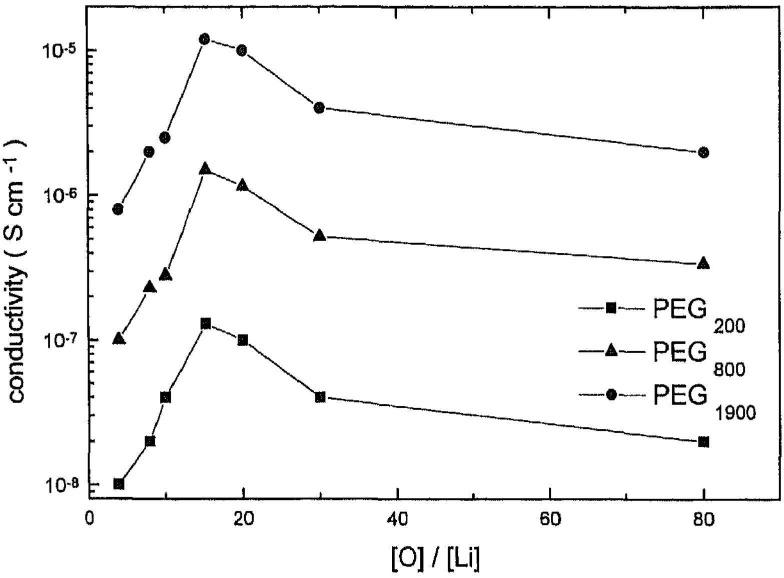

Fig. 1. Variation of the room temperature conductivity for chemically bonded hybrids silica-PEG$_n$, with $n = 200$, 800 and 1900 as a function of the [O]/[Li] ratio.

Table 1
Variation of σ_0 and the activation energy E_a as a function of the PEG$_n$ chain length for type-I materials determined for [O]/[Li] = 15

	Silica-PEG$_{200}$	Silica-PEG$_{800}$	Silica-PEG$_{1900}$
σ_0 (S cm^{-1})	9.6×10^{-1}	8.4×10^{-4}	3.3×10^{-2}
E_a (eV)	0.4	0.16	0.2

shown that the mobility of the polymer chain near the silica clusters is much lower than the mobility of the chain at longer distance. So, a hybrid with short PEG chains offers only a small area of the chain with high mobility, while for longer chains the region of high mobility is much higher. This phenomenon is responsible for the ionic conductivity results. Table 1 presents the variation of the activation energy and the σ_0 values, deduced for all samples from the Arrhenius law $\sigma = \sigma_0 \exp(-E_a/RT)$, as a function of the PEG chain length for type-I hybrids determined for [O]/[Li] = 15 (minimum values).

The effect of increasing the chain length on the mobility of the polymer in type-I material is also clearly observed in the temperature dependence of the NMR results. The motional narrowing of the ^{7}Li line width and the minimum of the ^{7}Li spin-lattice relaxation time T_1 occur at lower temperatures for longer polymer chains. This confirms that the polymer mobility increases as a function of the polymer chain length, as shown in Fig. 2 for silica-PEG$_{800}$ and silica-PEG$_{1900}$ samples.

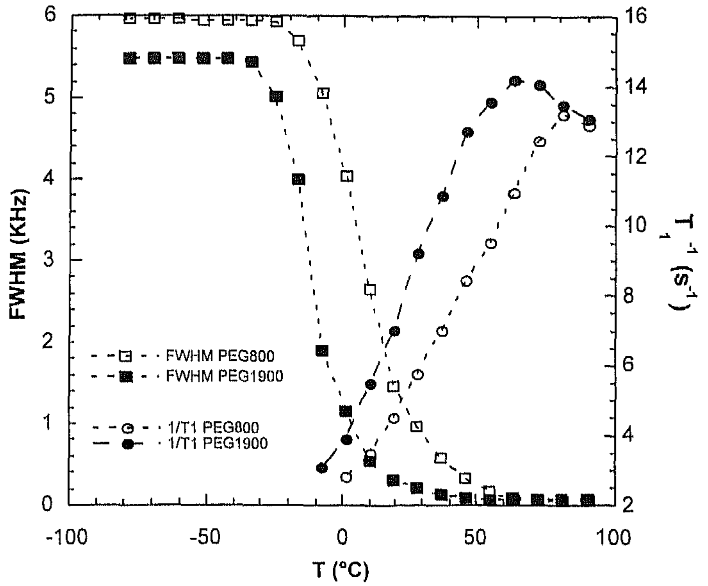

Fig. 2. Temperature dependence of the ^{7}Li linewidth and ^{7}Li spin-lattice relaxation time T_1 in type-I materials: silica-PEG$_{800}$ and silica-PEG$_{1900}$, both with [O]/[Li] = 4.

3.2. *Type II materials with weak physical bonds between the organic and inorganic network*

(a) *Effect of the lithium concentration*: Fig. 3 presents the variation of the room temperature conductivity σ_{amb} for the not chemically bonded hybrid silica-PEG$_{300}$ as a function of the ratio [O]/[Li] (where oxygens considered are only those of the ether type) and for different PEG/TEOS ratio (0.2, 0.4, 0.8 and 1). Once again, the overall shapes of the curves are similar but the values of σ_{amb} are much higher than those obtained with type-I materials. A maximum is also always observed but for $[\mathrm{O}]/[\mathrm{Li}] \cong 8$. This behavior is similar to that observed in most polymer electrolytes [8, 9], as only weak physical bonds (Van der Waals, hydrogen bonds) are present between the PEG and the SiO$_2$ network. The polymer chains have a higher mobilitythan in type-I materials and their immobilization by interactions with the Li$^+$ ions occurs consequently at higher lithium concentration.

(b) *Effect of the polymer chain length*: Table 2 presents the variation of σ_{amb}, σ_0 and E_a of the conductivity as a function of the PEG chain length for the not chemically bonded silica-PEG hybrids determined for [O]/[Li] = 4. σ_{amb} and, therefore, the PEG chain mobility increases when the polymer chain length decreases. Because of the absence of "strong" chemical bonds between both networks the polymeric phase has a "liquid-like" behavior [4, 6]. With this configuration the interaction between the polymer chains themselves is smaller when the chains are short so that their mobility is higher than that of long PEG chains.

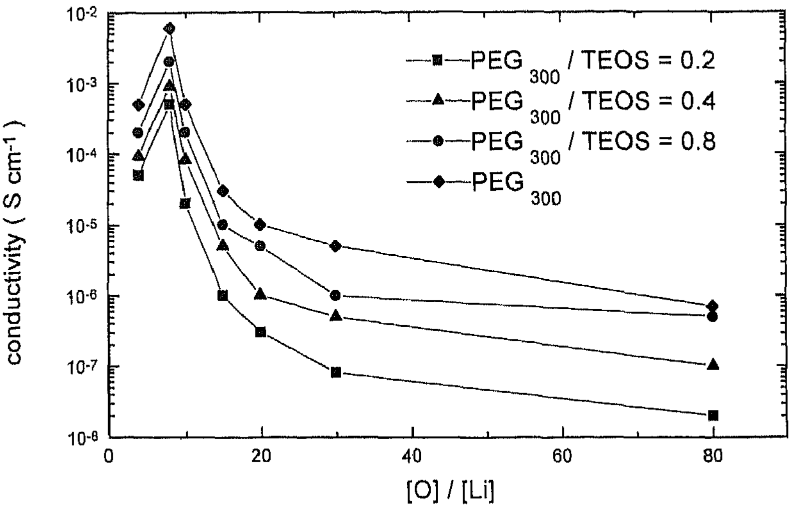

Fig. 3. Variation of room temperature conductivity, σ_{amb}, for the non-bonded hybrid silica-PEG$_{300}$ as a function of the ratio [O]/[Li] and various PEG/TEOS ratios.

Table 2
Variation of σ_0 and activation energy as a function of the PEG$_n$ chain length for type-II materials determined for [O]/[Li] = 4

	Silica-PEG$_{300}$	Silica-PEG$_{600}$	Silica-PEG$_{1000}$
PEG/TEOS (wt%)	40	40	40
σ_{amb} (S cm^{-1})	9.2×10^{-5}	3.5×10^{-6}	8.0×10^{-7}
σ_0 (S cm^{-1}) $T > 50°C$	6.6×10^{-4}	2.5×10^{-5}	2.2×10^{-3}
E_{a1} (eV) $T > 50°C$	0.05	0.05	0.2
E_{a2} (eV) $T < 50°C$	0.19	0.23	0.45

The variation of the conductivity with temperature shows discrepancies with a pure Arrhenius model. Two slopes are observed, with an intercept around 50°C for all systems with activation energies $0.05\text{ eV} < E_{a1} < 0.2\text{ eV}$ for $T > 50°C$ and $0.2\text{ eV} < E_{a2} < 0.5\text{ eV}$ for $T < 50°C$. Such behavior has also been observed in some polymers [11] and composites electrolytes [12] and interpreted as due to a partial crystallization and phase separation below a critical temperature. The chemical stability of type-II material is, therefore, lower than that of type I.

Again, the effect of the chain length on the mobility of the polymer in type-II material is shown by the NMR measurements. In this case, however, the motional narrowing of the ^{7}Li line width and the minimum of the ^{7}Li spin-lattice relaxation time T_1 that occur at higher temperatures for longer chains confirm that the chain mobility decreases with its length (Fig. 4).

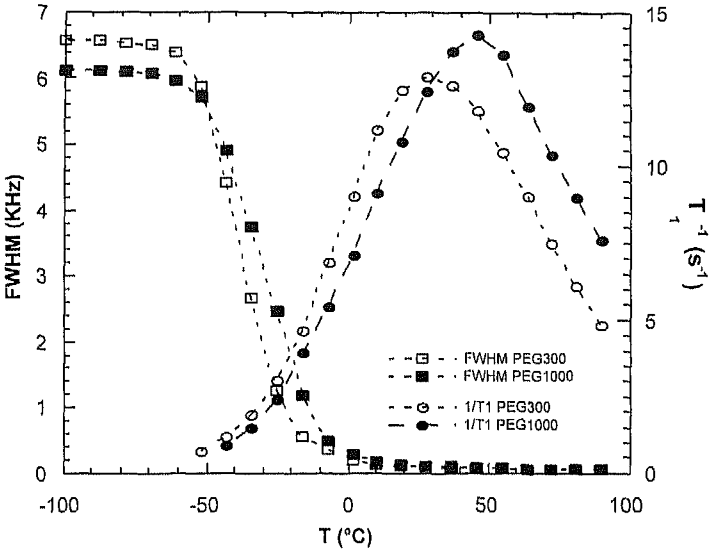

Fig. 4. Temperature dependence of the ^{7}Li line width and ^{7}Li spin-lattice relaxation time T_1 in the type-II materials: silica-PEG$_{300}$ and silica-PEG$_{1000}$, both with [O]/[Li] = 4.

Table 3
Variation of σ_0 and the activation energy as a function of the ratio PEG$_{1000}$/TEOS for type-II materials with [O]/[Li] = 4

	Silica-PEG$_{1000}$	Silica-PEG$_{1000}$	Silica-PEG$_{1000}$	Silica-PEG$_{1000}$
PEG/TEOS (wt%)	20	40	80	100
σ_0(Scm^{-1}) $T > 50$°C	1.1×10^{-3}	2.2×10^{-3}	4.3×10^{-4}	8.4×10^{-4}
E_{a1}(eV) $T > 50°$	0.2	0.2	0.14	0.14
E_{a2}(eV) $T < 50$°C	0.45	0.45	0.36	0.36

(c) *Effect of the polymer concentration*: The ionic conductivity σ_{amb} increases with the polymer concentration (Fig. 3). In samples with high-PEG concentration the influence of the silica network (Van der Waals or hydrogen interactions) is negligible for the "liquid-like" polymeric phase. When the volume of the PEG decreases, the influence of the interface between organic and inorganic domains becomes predominant and the mobility of the polymer chain is small. This influences the conductivity values. Table 3 presents the variation of σ_0 and of the activation energy as a function of the PEG/TEOS weight ratio for the not chemically bonded hybrid silica-PEG$_{1000}$ determined for the ratio [O]/[Li] = 4.

4. Conclusions

In type-I materials the ionic conductivity presents a maximum for [O]/[Li] = 15, while for type II and pure polymer electrolytes this occurs at [O]/[Li] = 8. For type

II the ionic conductivity increases with the polymer to silica weight ratio. Both types of materials present high-ionic conductivity values at ambient temperature and are consequently quite adequate to be used as Li^+-conducting electrolyte in all solid-state electrochemical devices. The temperature dependence of the line width and ionic conductivity at room temperature for the various samples show that for the bonded chains the mobility increases with chain length, while the opposite happens with the unbonded chains. The line width transition temperatures correspond to the glass transition temperatures, determined by other techniques. Analysis of the behavior of the minimum of T_1 of the same samples confirms the above results that are also consistent with the observed conductivity values. For some samples, a second narrowing is observed around 60°C, possibly related to the onset of an unbounded ion motion [13].

Acknowledgements

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