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SOL-GEL SYNTHESIS, THERMAL CHARACTERIZATION AND CONDUCTIVITY OF NEW GLASS-POLYMER SOLID ELECTROLYTES

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Abstract

Poly(ethylene oxide) (PEO) based-polymeric solid electrolytes are of growing interest for their applications in electrochemical devices. Their major limitations are structural and electrochemical stability, and low cationic transport number. A possible response to these problems is given by composite or nanostructured materials. We present sol-gel synthesis, thermal and electrical characterization of new electrolytes made of a composite glass-polymer matrix doped with $LiClO_4$ and $LiBF_4$. Emphasis to the critical aspects of preparation is given. We obtain a conductivity at room temperature better than 10^{-5} ohm^{-1} cm^{-1}, which is high enough to envisage technological applications.

Keywords: composites, lithium triborate, PEO, solid electrolytes

Introduction

During this last decade, hundredth ot polymeric electrolytes with a substantial conductivity at room temperature has been synthesized and characterized [1]. These materials find technological applications in electrochemical devices like batteries, sensors, super capacitors and SMART windows [2]. The most important family of polymeric electrolytes which has been developed during these years is that of salt-doped polyethers [3], like poly(ethylene oxide), PEO, and poly(propylene oxide), PPO. In the following, we mainly focus our attention on PEO systems.

At present, the most striking problems unresolved are long-term electrochemical stability of the electrode-electrolyte interface and, above all, the fulfilment of high energy density levels (~10^3 Wh kg^{-1}) which are necessary to envisage outstanding technological applications, for example in batteries for electric cars. These high current density values may be attained by raising the cation transport number, t^+.

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The development of "chimie douce" preparation techniques, such as sol-gel, has opened new interesting perspectives in the synthesis of composite and/or nanostructured materials (glass-ceramics, glass-polymers) whose physicochemical properties are by far predictable and, at some extent, even "tuneable" [4]. It is well known, on the other hand, that "classical" borate- or phosphate-based glassy electrolytes display an essentially cationic conductivity [5], whereas their use in electrochemical devices has been early envisaged [6]. It seems worthwhile, in this sense, to try the synthesis of composite electrolytes where the host matrix is made of a glass and of a polymer with a low glass transition temperature, T_g. The glass could enhance the cationic transport number and the stability properties, whereas the amorphous, low-T_g, polymer will give rubbery compliance and a high conductivity background at room temperature. In addition, a "strong" glass could contribute to hinder the long-term crystallization at the polymer, which is another problem of technological relevance.

In this paper we will discuss sol-gel synthesis, thermal and electrical characterization of new solid electrolytes obtained by doping with different lithium salts a host composite matrix made of PEO and a lithium triborate glass $Li_2O{:}3B_2O_3$, with a ratio n =O(EO)/Li (glass) =8 (in the following referred as PEOGL matrix). As a first step, we will describe in detail the problems related to the sol-gel preparation of the glass, and we will present its partial thermal and structural characterization. Emphasis will be given to the purity requisites of the starting materials and to the conditions under which the synthesis was performed. Different films have been prepared by doping the PEOGL matrix with $LiClO_4$ or $LiBF_4$. We will discuss the properties of these solid electrolytes in terms of the ratio n'=O (PEO)/Li (lithium salt).

Experimental details

Raw materials conditioning

The powder of pure PEO (BDH Ltd., Polyox WSR-301, molecular weight (600.000) has been dried overnight at 50°C in a oven under vacuum (10^{-2} torr) and kept in a desiccator. Anhydrous $LiBF_4$ (Fluka, 98%) was dried 24 h at 120°C in a oven under vacuum and then kept in a desiccator. Anhydrous $LiClO_4$ (Aldrich, 95%) was particularly critical to prepare. Figure 1 shows, over the same scale, the DSC curves at the salt as received (a), after 72 h of annealing in a oven at 180°C (b), and after scan up to 300°C (i.e. above the salt melting point) in the DSC itself (c). The overlapping endotherms appearing in curves a) and b) in the range 120–180°C are due to some water of crystallization which is very hard to remove. As a matter ot fact, it is possible to extract all water in a DSC experiment performed on low mass samples (~20 mg), as clearly demonstrated by curve c) where only the $LiClO_4$ melting endotherm at ~248°C [7]

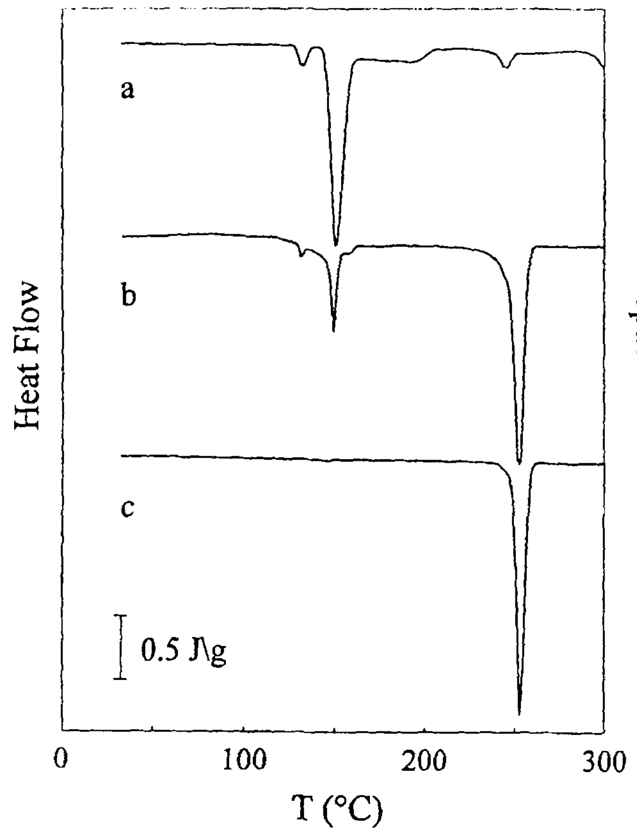


Fig. 1 DSC curves of the $LiClO_4$ as received (a), after 72 h of annealing in an oven at 180°C (b), and after a DSC scan up to 300°C (c)

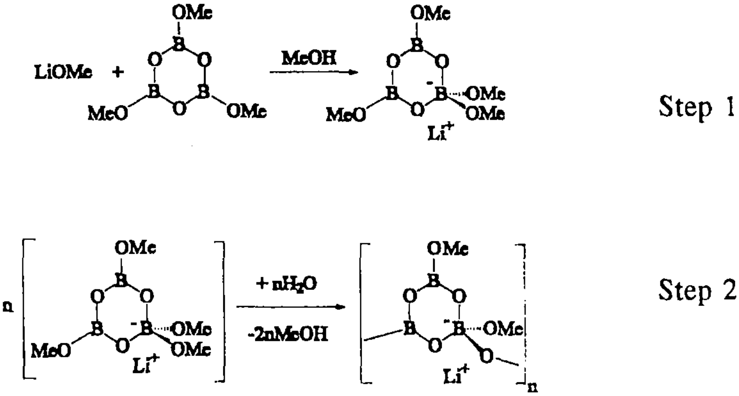
is present. In the case of larger masses heated in a conventional oven, however, the kinetics of extraction resulted very slow also at 180°C, while for higher temperatures the sample underwent thermal decomposition. To enhance the stripping kinetics, the oven was slightly depressurized and fluxed with a little flow of dry nitrogen: this procedure seemed to work slightly better than the conventional thermal treatment under vacuum. A TG measurement revealed that $LiClO_4$ heated 72 h at 180°C had yet retained ~2%wt of crystallized water.

Trimethoxyboroxine (Aldrich) and lithium methoxide (Aldrich, 98%) were stored in the dry box immediately after purchase, opened and always kept there.

Glass preparation

Lithium triborate, $Li_2O{:}3B_2O_3$, was prepared following a sol-gel route in dry atmosphere (Dew Point ~–50°C, corresponding to ~38 ppm.V. of H_2O) by slowly adding 0.090 moles of trimethoxyboroxine to a solution of 0.085 moles of lithium methoxide in 32 cm^2 of absolute methanol (less than 50 ppm H_2O, Aldrich, 99%). A little excess of trimethoxyboroxine was added to compensate for reaction with water. The sol was carefully stirred 1 hour in dry box and then left to hydrolyze in ambient atmosphere (~70% relative humidity) at room temperature for 2 days, until complete gelation occurred. During gelation, we observed formation of short and fragile fibres which could be extracted and dried. The gel was then completely dried at room temperature in air and treated at 90°C for 24 h in an oven to obtain a white powder. A part of the triborate glass was dried overnight at 350°C to evacuate residual methoxy groups (see Results).

The reaction followed the two-steps scheme proposed by Venkatasubramanian *et al.* [8], where the first step is the complexation of trimethoxyboroxine with lithium methoxide, and the second step is the hydrolysis and polycondensation to form the polymer network:



We stress the importance to perform the first step in a very dry atmosphere and using a water-free solvent. If these conditions are not fully satisfied, a complexation occurs between trimethoxyboroxine and water, which causes deposition of boric acid and a boron non-stoichiometry in the final product. In case of standard methanol as solvent, and operating with a Dew Point of –20°C (corresponding to ~1000 ppm.V. H_2O), we found a boron non-stoichiometry of the order of 20 mol%.

The composite PEOGL matrix and the doping

PEOGL matrix has been prepared with a PEO-glass molar ratio $n = 8$. This ratio was chosen in analogy with the one that assured the best transport properties in the case of a PEO-$Na_2O{:}3B_2O_3$ matrix [9]. PEO has been dissolved in hot methanol and the solution stirred 1 h. Then, the proper amount of triborate glass powder was added to the solution and stirred 3 days up to its complete dissolution.

Proper amounts of $LiClO_4$ or $LiBF_4$ were added to the solutions, at ambient atmosphere, in order to obtain compositions $n'= 2, 8, 20$, where n' is defined as the ratio O (PEO)/Li^+ (salt). Each solution was stirred 48 h at rt and then cast on a Teflon plate in order to slowly evaporate the solvent. Samples were finally dried under vacuum, with the following thermal cycle: i) 12 h at 30°C, ii) 12 h at 40°C, iii) 2 days at 55°C. The obtained films were homogeneous, with thickness varying from 0.1 mm to 1 mm. They were kept into a desiccator before the measurements.

Apparatuses

TG and DSC measurements were performed on samples of about 20 mg under N_2 flow, using DuPont units 951 and 910, respectively, interfaced to a TA2000 Thermal Analysis System (TA Instruments, USA). Some samples have been studied with a Modulated DSC 2970 (MDSC^{TM}, TA Instruments, USA) [10], which under proper conditions is able to separate thermodynamic reversible phenomena from irreversible ones (see, for example [11]).

Fourier Transform Infrared Spectroscopy associated with Thermogravimetric analysis (TG-FTIR) was performed using a Nicolet 730 FT-IR spectrometer fitted with a MTEC 200 Photoacoustic Detector.

Powder X-rays diffraction patterns have been collected with a Philips PW 1710 powder diffractometer, equipped with a Philips PW 1050 vertical goniometer and a graphite crystal monochromator (CuK_α radiation).

Conductivity measurements have been carried out with the Impedance Spectroscopy (IS) method, using a Solartron 1260 Frequency Response Analyzer (FRA), in the temperature range 26–150°C and in the frequency range 1 Hz–1 MHz. Disk-shaped samples have been pressed between two silver plates and connected to the FRA with coaxial cables. The measurements have been performed under primary vacuum in a Büchi TO-50 oven. Before measurements the samples have been heated at 70°C under vacuum, then kept 15 h at rt always under vacuum. Conductivity data have been collected with a Basic program running on a 80486 PC-compatible.

Results and discussion

Figure 2 shows the X-rays powder diffractogram at room temperature of the lithium triborate such us prepared. The glassy nature of the compound is clearly evidenced by the absence of reflection peaks. Figure 3 shows the MDSC^{TM} results: the reversing heat flow signal (dotted line) reveals a glass transition at ~480°C, in good agreement with the literature data on lithium triborate glass obtained by quenching a melt [12]. For a detailed discussion about the meaning of reversing and non-reversing components in a MDSC^{TM} run, and about the in-

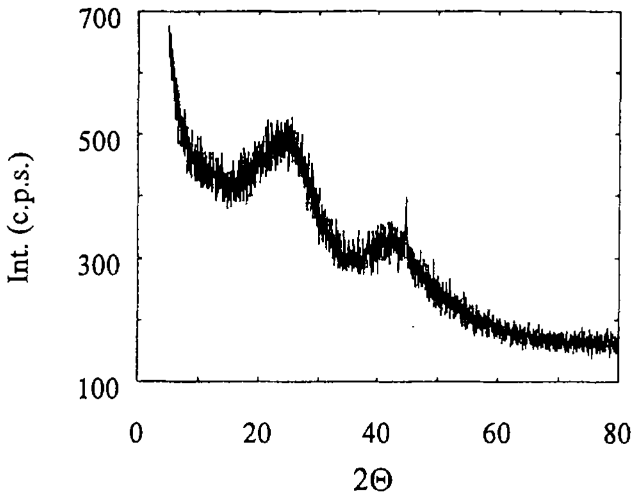


Fig. 2 X-rays powder diffractogram at room temperature of lithium triborate glass

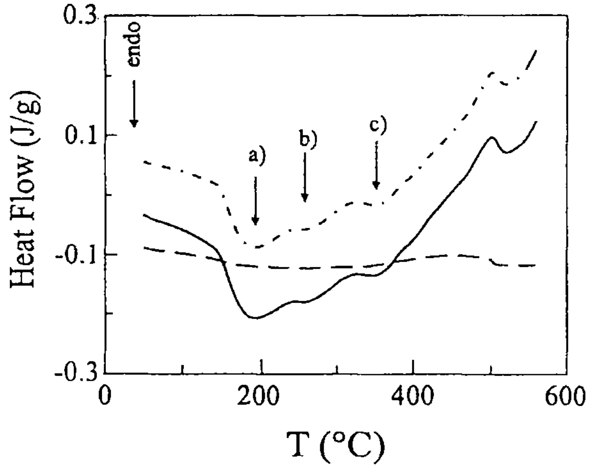


Fig. 3 MDSC^{TM} curves of lithium triborate glass: total heat flow signal (solid line), reversing heat flow signal (dotted line), and non-reversing heat flow signal (dashed line). The meaning of the arrows a, b and c is explained in the text

fluence of the experimental modulation parameters see Ref. [11]. The total heat flow curve (solid line), which corresponds to the signal obtained by a conventional DSC, displays three broad and partially overlapping endothermic phenomena at ~200°C (labelled a), ~270°C (b) and ~350°C (c). These broad peaks behave the same in the non-reversing heat flow (dashed line) and may be attributed to the loss of water (a) and of methoxy groups attached to the boroxol rings (b and c, see TG-FTIR results).

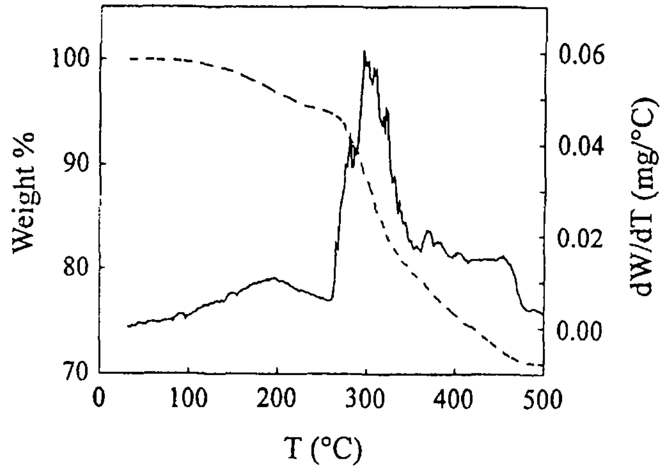


Fig. 4 Thermogravimetric curve of lithium triborate glass (a) and its derivative over temperature (b)

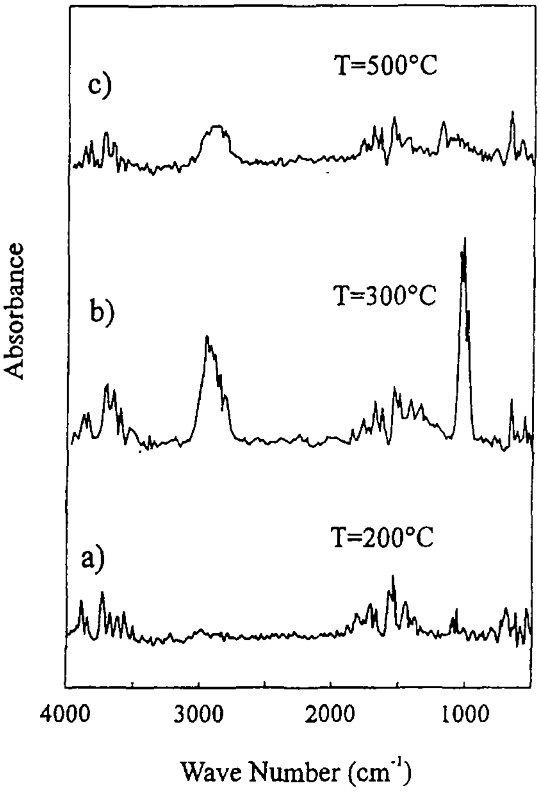


Fig. 5 TG-FTIR absorption spectra of lithium triborate glass at 200°C (a), at 300°C (b) and at 500°C (c)

Figure 4 shows, for lithium triborate, the TG curve (a) and its derivative over temperature (b). During a scan up to 500°C, TG shows a loss of ~29 wt% which is in good agreement with a theoretical value of 27.9 wt% if each boroxol monomer released two methoxy groups. The difference is accounted for by considering loss of residual water below 200°C (see below). The deriva-

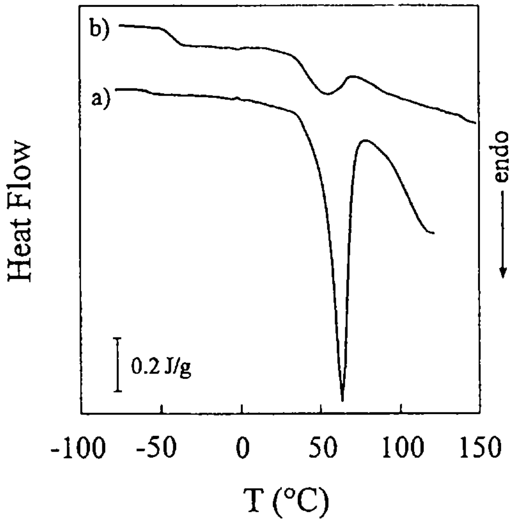


Fig. 6 DSC curves for the PEOGL matrix doped with $LiBF_4$: a) $n'=20$, b) $n'=8$

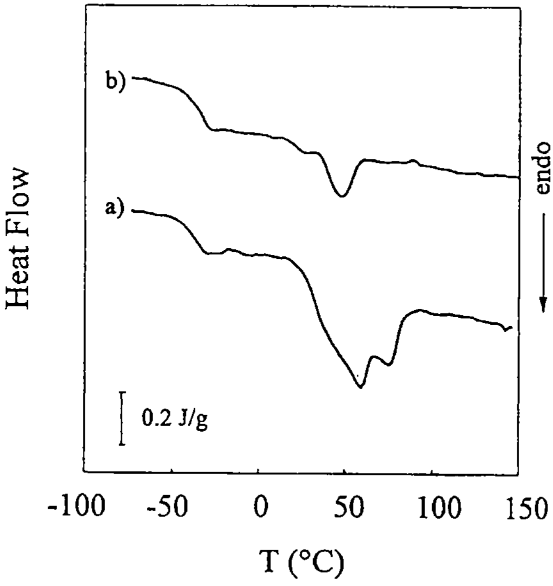


Fig. 7 DSC curves of the PEOGL matrix doped with $LiClO_4$: a) $n'= 20$, b) $n'=8$

tive curve highlights three distinct losses at the temperatures where MDSC™ displays the broad endotherms.

Figure 5 shows the IR absorption spectra of the gaseous products of the TG run at 200°C (part a), at 300°C (part b) and at 500°C (part c). The IR spectrum reported in (a) displays absorptions in the region 1350–1500 cm^{-1} that are attributed to O–H bending [13], and in the region 3600–4000 cm^{-1} (O–H stretching): this calls for the presence of water in the evolution gases. The spectrum reported in part b presents, in addition to the O–H peaks, two other intense absorption bands at ~1050 cm^{-1} (C–O stretching) and ~2900 cm^{-1} (C–H stretching of methyl groups) that clearly indicate the presence of methanol. Finally, the spectrum displayed in c) reveals that the gaseous emission has practically ceased at 500°C, in agreement with TG.

Figure 6 shows the DSC curves for the PEOGL matrix doped with $LiBF_4$. Curve a) refers to $n'=20$ and curve b) to $n'=8$. Samples 8:1 and 20:1 display glass transitions near –40°C and –60°C, respectively. The endothermic phenomena above rt are due to the melting of the residual crystalline PEO.

Figure 7 shows, over the same scale, the DSC curves of the PEOGL matrix doped with $LiClO_4$. Curve a) refers to $n'=20$ and curve b) to $n'=8$. Glass transitions are always well-evident in the region between –50°C and –40°C. All samples display endotherms near ~60°C, which may be related to the melting of the residual crystalline PEO. This phenomenon, however, is very small for $n'=8$.

Figure 8 shows the powder X-rays diffractograms of PEOGL-$LiBF_4$ 8:1 (curve a), PEOGL-$LiClO_4$ 8:1 (curve b), PEOGL-$LiBF_4$ 20:1 (curve c), and

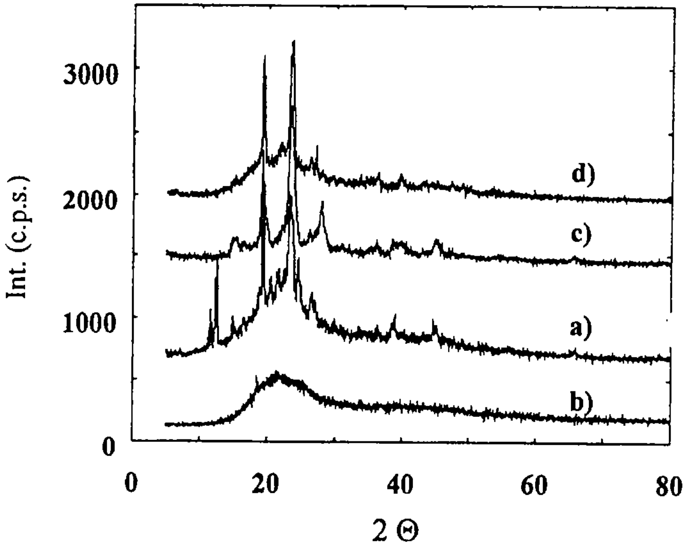


Fig. 8 Powder X-rays diffractograms of PEOGL-$LiBF_4$ 8:1 (a), PEOGL-$LiClO_4$ 8:1 (b). PEOGL-$LiBF_4$ 20:1 (c), and PEOGL-$LiClO_4$ 20:1 (d)

PEOGL-LiClO$_4$ 20:1 (curve d). A comparison between curves c) and d) shows that the two anions give origin to different crystalline structures, and that ClO_4^- determines a more pronounced amorphous background, which is in agreement with our DSC results. The behavioural differences between the two salts become dramatically evident when comparing the films $n'=8$:PEOGL-LiBF$_4$ retains a crystalline portion, whereas the one doped with LiClO$_4$ is totally amorphous, as predicted by DSC (Fig. 7b). We recall that the composition $n'=8$ roughly corresponds to the eutectic in the phase diagram of the binary system PEO-LiClO$_4$ [7, 14].

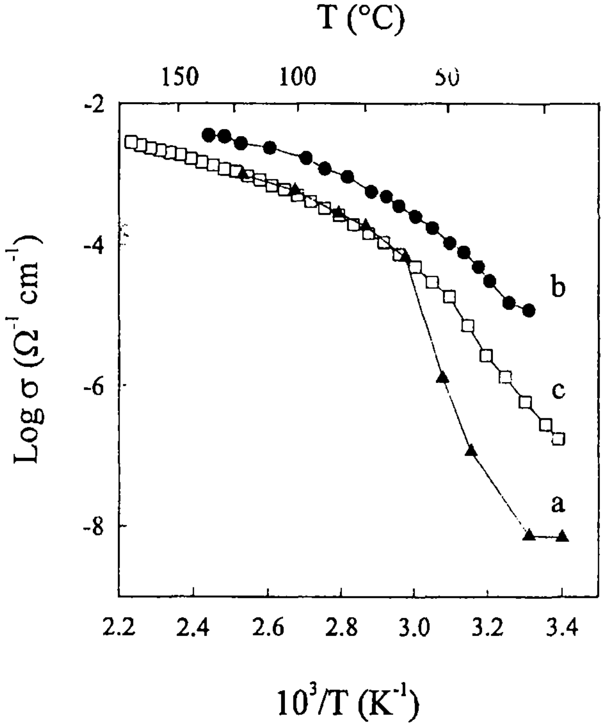


Fig. 9 Conductivity vs. temperature of PEOGL-LiBF$_4$ 8:1 (a), PEOGL-LiClO$_4$ 8:1 (b), and PEO-LiClO$_4$ 8:1 (c)

Figure 9, finally, shows the conductivity *vs*. temperature of PEOGL-LiBF$_4$ 8:1 (curve a), PEOGL-LiClO$_4$ 8:1 (curve b), and PEO-LiClO$_4$ 8:1 (curve c) which is taken as a reference [14]. Curve a) displays a singularity near the melting point of crystalline PEO at ~60°C, according with our X-rays and DSC findings. On the contrary, PEOGL-LiClO$_4$ 8:1 does not show the discontinuity and has a conductivity higher than that of the reference curve c). This composition displays a conductivity at rt which is high enough to envisage applications in solid-state electrochemical devices.

Conclusions

We have presented sol-gel synthesis, electrical and thermal characterization of new solid electrolytes based on a composite glass-polymer host matrix, which has been doped with $LiClO_4$ or $LiBF_4$. We have put into evidence some critical aspects of the preparation, in particular the ones related with moisture and the purity of raw materials. A detailed characterization of the triborate glass obtained with a sol-gel route has been given. Our findings show that $LiClO_4$ behaves better than $LiBF_4$ in doping our PEOGL matrix. In particular, the perchlorate ion assures an almost complete amorphization of the matrix structure, at least near the eutectic region, while the fluoroborate one does not work so well.

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