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Sol-gel derived Li-ion conducting polymer electrolytes

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Organic-inorganic hybrids have recently become a remarkable family of amorphous polymer materials with promising potential applications. In the present study, sol-gel derived organic-inorganic hybrid electrolytes doped with lithium salts (LiCl, $LiClO_4$) were produced from inorganic and organic precursors such as tetraethyl orthosilicate, poly(ethylene oxide), poly(ethylene glycol), propylene oxide, propylene carbonate, ethylene glycol, and 1,2-propylene glycol. The hybrid electrolytes were obtained in the form of flexible or glassy materials depending on the composition and heat treatment temperature (ranging from 80 to 125 °C). The morphology, structure and elemental chemical composition of the electrolytes obtained were examined by scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM/EDS), FTIR spectroscopy, and X-ray diffraction (XRD). Infrared spectroscopy and SEM observation results indicate that the structural properties of the synthesized materials are significantly influenced by organic additives and the sol-gel preparation procedure. The formation of organic group –O–Si linkages was confirmed by infrared spectra in all of the electrolytes obtained. The results of FTIR analysis are in a good agreement with ^{13}C and ^{1}H MAS NMR spectroscopy measurements performed for the hydrolysed sols immediately before the gel transformation process and at early gel stages. These results have revealed an enhanced duration of the cross-linking process in the species prepared with low molecular mass glycols. Cells in an electrochromic window arrangement were prepared in order to observe the photometric and cyclic voltammetry characteristics of thin-film electrochromic systems with the investigated hybrid materials employed as electrolytes. The results indicate that the inorganic-organic hybrids synthesized in this work are promising electrolytes for thin film electrochromic systems based on WO_3.

Key words: *organic-inorganic hybrid; sol-gel; ionic conductivity; Li^+-conductive electrolytes*

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1. Introduction

The development of high conductive solid electrolytes for applications in advanced electrochemical and optoelectronic devices such as lithium rechargeable batteries and electrochromic windows and displays, have recently focused extensive research efforts on materials with high ionic conductivity at low temperatures [1–4].

Polymer electrolytes based on complexes of poly-ethers with alkali metal salts and especially poly(ethylene oxide) (PEO) which act as host matrices for lithium salts have been extensively studied for such applications in light of their advantageous chemical and mechanical resistance and excellent contact with electrode materials. The main disadvantage of using polymer electrolytes in electronic and optoelectronic devices is their relatively high content of crystalline phases resulting in low room-temperature ionic conductivity. Low-temperature ionic conductivity in polymers is known to be almost exclusively dependent on the mobility of ionic charge carriers in the amorphous regions and due to this, much research effort has been directed towards the possible enlargement of amorphous phase content in polymer electrolytes [5–7]. In recent years, there have been reports on so-called composite polymer electrolytes with ionic conductivity improved due to the addition of liquid plasticisers and/or application of solid fillers, advantageously in the form of fine ceramic particles [8–10]. Such modifications of polymer electrolytes morphology have proved to be an effective way to suppress the tendency for crystallization. It seems to be more suitable, however, for rechargeable fuel cells rather than electrochromic window systems, which are required to be transparent and highly colourless in the bleached state [1–4, 11].

On the other hand, transparent amorphous materials, both in monolithic and thin film forms, can be relatively easily obtained by using a sol-gel method [12–14]. The organic modification of glasses and the other sol-gel derived materials is possible, as sol preparation and the sol-gel process proceed at ambient and negligibly increased temperatures, respectively. Due to, a great number of organic additives were successfully incorporated into gels from the solutions containing gel precursors in mixtures with the organic compounds [15–22]. Sol-gel process have proved to be a useful tool for obtaining new families of organically modified ceramics (ormocers) and silicate materials (ormosils), as well as organically modified electrolytes (ormolytes) in which organic groups can be included either by the co-polymerisation of organic monomers with metal alkoxides or by the co-condensation of modified alkoxides [17–22]. Among others, Malzbender et al. [15] have reported on organic-inorganic hybrid coatings for float glass, where the coating fluid contained methyltrimethoxysilane (MTMS). Georgi et al. [16] have studied the influence of glutardialdehyde, 3,4-dimethoxybenzaldehyde, and aminocaproic acid additives on the properties of sol-gel layers derived from tetraethoxysilane (TEOS).

The sol-gel method has also proved to be an excellent process for preparation of silica- or silica-based gels. Silica gels contain a large number of micro-pores, which makes them useful in many various applications [23–25]. In addition, the pore structure and size can be controlled by the parameters of the sol-gel process, such as the atmosphere and rate of solvent evaporation during the first stages of drying and parameters during subsequent heat treatment.

Porous gel materials can trap or be easily filled and/or processed with liquids and gases. Matsuda et al. [26] have studied the proton conductivity of sol-gel derived porous silica gels impregnated with sulphuric acid. On the other hand, it is known that polymers with incorporated liquid electrolytes, i.e. containing plasticisers or porous gelled polymer electrolytes, generally exhibit ionic conductivity at room temperature being about 10^{-3} S·cm^{-1} higher than that of “dry” polymer electrolytes (such as PEO -lithium salt solid complexes). Matrices of hybrid electrolytes or those derived from porous silica gels can be expected to trap a liquid phase with dissolved lithium salt. Due to this, such systems can be considered to consist of a liquid electrolyte dispersed in a solid matrix, with the lithium and counter ions migrating throughout the solvent [27].

Many kinds of polymers have been proposed as components of gel polymers and sol-gel derived hybrid electrolytes, including polyacrylonitrile (PAN), poly(ethylene oxide) (PEO), poly(tetramethylene oxide) (PTMO), poly(methyl methacrylate) (PMMA), polyethylene glycol (PEG), polypropylene glycol (PPG), poly(vinylidene fluoride) (PVDF), some network polymers prepared by cross-linking reactions, and mixtures of polymers from these two groups [28–31]. Among those organic compounds, polyether polymers have a favourable feature of being miscible with many kinds of liquid electrolytes used in Li batteries [29, 31]. In addition, the preparation of hybrid gel electrolytes with polyethers as organic parts is relatively easy. Dahmouche et al. [32, 33] have investigated two families of Li^+-conducting ormolytes. The first family, with ionic conductivity higher than 10^{-4} S·m^{-1} at room temperature and exhibiting chemical bonds between the organic and inorganic phase, was obtained from a mixture of 3-isocyanatopropyltriethoxysilane, O,O′-bis-(2-aminopropyl)-polyethylene glycol (or O,O′-bis-(2-aminopropyl)-polypropylene glycol, and lithium salt. In the other family, prepared by ultrasonic or traditional sol-gel processes from the mixture of tetraethyl orthosilicate (TEOS), polyethylene glycol (PEG), and lithium salt ($LiClO_4$), the organic and inorganic parts were not chemically bonded and ionic conductivities of up to 10^{-2} S·m^{-1} were obtained at room temperature with a silica-PEG$_{300}$ system (PEG/TEOS = 40% in weight). Chaker et al. [34] have reported on siloxane-poly-(propylene oxide) (PPO, with 2000 and 4000 g/mol molecular weight) hybrid electrolytes doped with sodium perchlorate ($NaClO_4$), obtained by the sol-gel method and exhibiting the ionic conductivity of $8{,}9\times10^{-4}$ S·cm^{-1} at room temperature. Poly-(ethylene oxide)-based gel-type polymer electrolytes doped with lithium perchlorate ($LiClO_4$), containing nanoscale-fumed SiO_2 dispersed in acetonitrile and showing ionic conductivity higher than 10^{-3} S·cm^{-1} at room temperature have been obtained by Aihara et al. [35].

In general, organic-inorganic hybrids have proved to be a remarkable family of amorphous polymeric materials with promising potential applications.

The goal of this work was to obtain sol-gel derived organic-inorganic hybrid electrolytes doped with lithium salt (LiCl, $LiClO_4$). The electrolytes were produced from solutions containing tetraethyl orthosilicate (TEOS) as an inorganic precursor of SiO_2 gels and poly(ethylene oxide) (PEO) or poly(ethylene glycol) (PEG), together with propylene oxide (PO), propylene carbonate (PC), ethylene glycol (EG), and 1,2-propylene glycol (PG) as low-molecular-weight organic additives. The structural properties of the organic-inorganic hybrids were compared with those of lithium doped or pure (without lithium salt doping) silica gels prepared under the same conditions and using the same sol-gel procedure employed for obtaining the inorganic parts of hybrid electrolytes.

2. Experimental

Based on earlier results for the same sol-gel procedures [28], the sols for preparing silica gels were produced by mixing TEOS $Si(OC_2H_5)_4$ (Merck), distilled water, and 36.6% HCl as a catalyst. HCl was added drop by drop until pH = 2 was reached. Two receipts were used: the first, for PEO-containing sols, with the volume ratio of TEOS :distilled water:ethanol being 1:1:2.5, and the other, for sols with glycols, with the molar ratio of TEOS:distilled water being 1:4. Solutions of PEO–$(CH_2CH_2O)_n$ (nominal molar weight M_w = 600 000, Aldrich) in organic solvents (dichloromethane, ethanol, or acetonitrile C_2H_3N), and aqueous or ethanol solutions of poly(ethylene glycol) (nominal molar weight M_w = 6000 or 15 000, Fluka, Aldrich, respectively) with appropriate additives (Table 1) of propylene carbonate PC C_4H_6O (Merck), propylene oxide PO C_3H_6O (M_w = 58.08, Merck), ethylene glycol EG $HO(C_2H_4O)_nH$ (M_w = 62.08, Merck), 1,2-propylene glycol PG $CH_3{\cdot}CH(OH){\cdot}CH_2OH$ (M_w = 76.10, Fluka), and lithium salts ($LiClO_4$ or LiCl, Merck) with a weight ratio of about 0.02 and 0.03 with respect to the mass of fresh gels were used.

The chemical components and solvents employed were of at least reagent grade. The salts for doping, before being added to the solution of TEOS or to the mixtures of TEOS with other components, were dissolved in the entire calculated amount of water, ethanol, or PC. The sols containing TEOS were vigorously stirred for about one hour before being mixed with the polymer solution, and the resulting sols were stirred for the next 2.5–3.0 hours at the temperatures in the range of 50–55 °C, until the end of the hydrolysis reaction, namely after about 30 minutes. The mass fractions of the organic additions were calculated with respect to the resulting content of organic part in the gels of about 20 wt. %, with weight concentration of PEO or PEG to low-molecular-weight organic additives equal to 1, and molar ratio of low-molecular-weight monomers equal to 1.

The solutions of TEOS and polymers with appropriate solvents, before being used, were first stirred for 2 days and then baked and degassed by vacuum heating at 50 °C for 3–4 hours.

Table 1. Components of the starting solutions (quality composition) of the investigated gels

Sample	Components/solvents	Salt/fraction	Appearance, remarks
R	TEOS	$LiClO_4$/PC/0.03	silica glass, colourless, completely transparent
O	TEOS, 1,2-PG , PC	LiCl/ H_2O /0.02	organic glass, colourless, completely transparent
S	TEOS, PEO/CH_3CN, PC, PO	$LiClO_4$/PC/0.03	organic glass, slightly opalescent, colourless
Y	TEOS, PEG (6000)/H_2O	$LiClO_4$/PC/0.02	organic glass, slightly opalescent, colourless
T	TEOS, PEG(15000)/CH_2Cl_2, 1,2-PG, PO, PC	LiCl /H_2O/0.03	organic glass, colourless, transparent
X	TEOS, EG, 1,2-PG	$LiClO_4$/PC/0.03	organic glass, colourless, completely transparent
Z	TEOS, PEG (15000), PEO/CH_2Cl_2, 1,2-PG	LiCl /H_2O/0.02	organic glass, slightly opalescent, colourless

No precipitations or liquid remains were observed in the organic-inorganic materials after gelation was complete. All the gels obtained were kept in closed containers for two weeks and then dried for a week at ambient temperature and for three hours in an electric drier at 80–125 °C. The same treatment was applied to gels prepared as thin layers, by casting immediately onto glass sheets coated with thin films of SnO_2:F and WO_3 or NiO. They were then used as transparent electrolytes in the electrochemical cells of an electrochromic window, and their suitability for such applications was examined. Thin electrochromic films of WO_3 and NiO on glass were obtained by pyrolysis at the temperatures in the range of 750–800 °C, using acetylacetonates of the appropriate metals as precursors. The detailed procedures of metal oxide film preparation have been described earlier [36].

The morphology, elemental chemical composition, and crystalline character of the hybrid electrolytes and silica gels obtained in this work were examined by SEM/EDS using scanning electron microscopy (JEOL JSM 5400) equipped with energy dispersive X-ray spectroscopy (LINK An 10/5) and X-ray diffraction (XRD 7, Seiffert diffractometer). Structural properties were investigated with FTIR spectroscopy (BIO-RAD FTS 60 VM, on samples prepared by the KBr pellet technique). ^{13}C, ^{1}H MAS NMR (Bruker AMX 500 spectrometer) measurements were made for sols at three stages (two days after preparing the mixtures, and subsequently a week and two weeks later). Spectral transmittance (UV/VIS/NIR, Jasco-570 spectrometer) and current-voltage (CV) characteristics were recorded in systems consisting of two glass sheetscoated with metal oxides and layers of the hybrid electrolytes under investigation in an electrochromic window arrangement. The WO_3 and NiO thin metal films and electrolyte layers, as measured with a “Talystep” (Taylor Hobson) stylus microprofilometer, were about 140 nm and 170 nm thick, respectively, while the layers of electrolytes were about 6 μm thick. Transparent electrodes were prepared with their conductive paths coated with Ag-paste on the face side. The electrodes were placed along one edge of the sample, but opposite to each other and with platinum wires fixed to the paths with Ag-paste. When sandwiched with an examined electrolyte, all the cells under investigation were sealed around the edges with silicon sealant. Low voltage

(±) polarized d.c. potential was applied to the cells through a potentiostat/galvanostat as the power source. A rectangular pulse of current was supplied using a galvanostat and a pulse generator. The d.c. electrical conductivity was measured by using domestically set equipment, with a potentiostat and four-point probe included. The current and potential differences for each pair of contacts between the probe and examined sample were monitored with a high impedance (larger than 1000 MΩ) ammeter and voltmeter. Specific surface area and porosity were measured by N_2 adsorption at 77 K, using the BET and BJH equations, respectively).

3. Results and discussion

The names and appearance of the hybrid gel materials obtained are given in Table 1. The hybrid gels and silica gels prepared in order to compare their properties with those of hybrids were obtained in the form of the monolithic, colourless transparent discs with various thicknesses and diameters in the range of 20–50 mm. The hybrid materials were also obtained in the form of thin layers, immediately cast on glass coated with electrochromic thin metal oxide films. All the obtained hybrid electrolytes proved to be amorphous under XRD examination. The XRD patterns of typical hybrid electrolytes obtained in this work, named O, X and Y, are shown in Fig. 1.

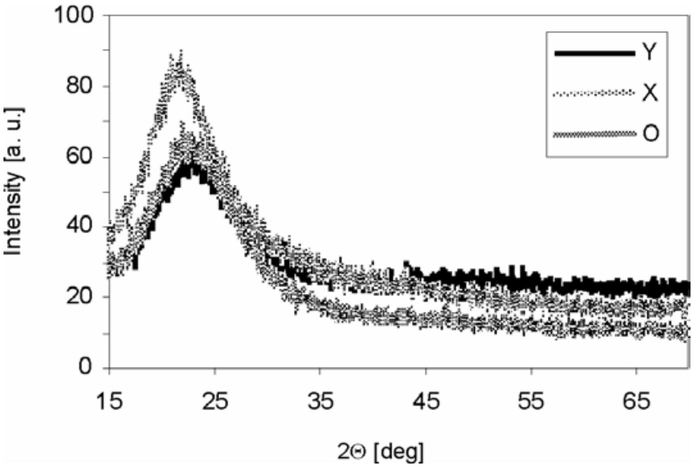

Fig. 1. X-ray diffraction patterns for sol-gel derived hybrid materials: O, X and Y

The morphologies of the hybrids and silica gels under investigation were observed using SEM/EDX. In Figure 2, planar-view SEM images of the hybrid gels (a–e) and silica gel doped with $LiClO_4$/PC (f) are shown.

FTIR spectra of silica-gel-derived hybrid materials, as well as silica gels, are shown in Fig. 3, and the assignments of the characteristic absorption bands are given in Table 2.

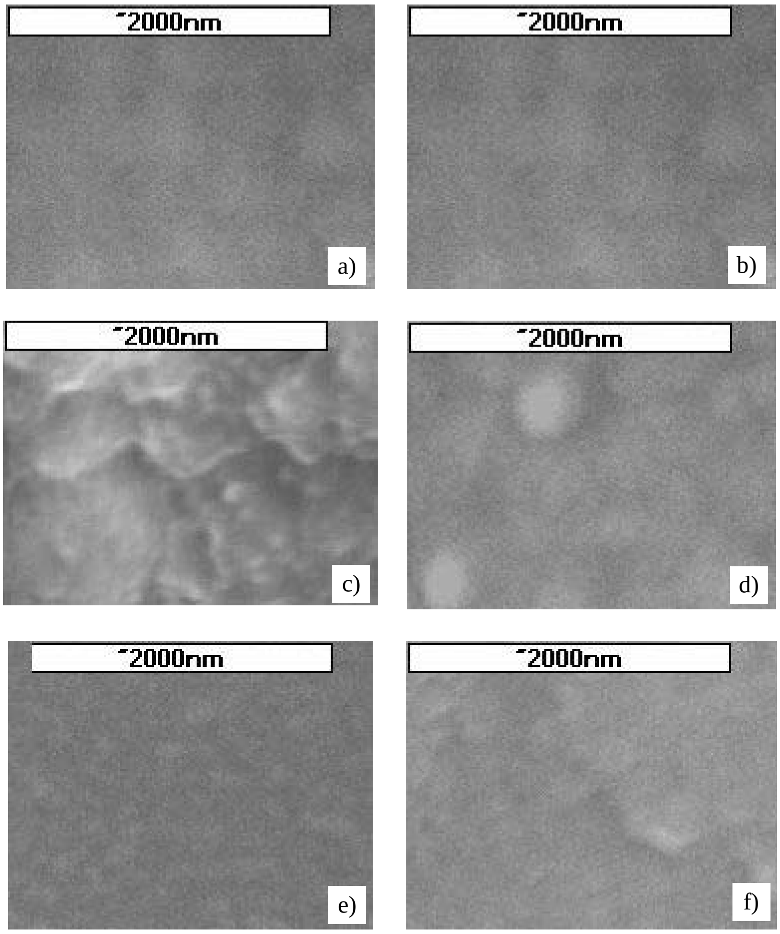

Fig. 2. SEM planar view images of hybrid organic-inorganic electrolytes:
a) S, b) T, c) X, d) Y, e) Z and f) R: silica gel doped with $LiClO_4$ dissolved in PC (x = 0.03)

Spectroscopic FTIR investigations (Fig. 3, Table 2) have revealed the presence of absorption bands characteristic of silicon–oxygen bonds, organic groups, and structural species connected to lithium bonding. Bands characteristic of water, both in the molecular (at about 3400 cm^{-1}) and adsorbed form (at about 1620 cm^{-1}) are also observed. Absorption bands in the wave number range 624–778 can be assumed to originate from organic structures ordered in molecular groups and in the presence of lithium atoms, but without phase separation or crystallization. Absorption bands at about 630 cm^{-1} can be ascribed to ClO_4^-. The propylene oxide absorption band is also localized around that wave number [37]. The absorption band at about 782 cm^{-1} is characteristic for hybrid gels and, according to Gunzler and Gremlich [38], can be ascribed to vibrations of the O-Si-C_nH_m species. It can therefore be considered as evidence of hybrid structure formation in the gels under investigation, with the organic and inorganic parts being connected to each other by oxygen bridges. In the spectra of all the

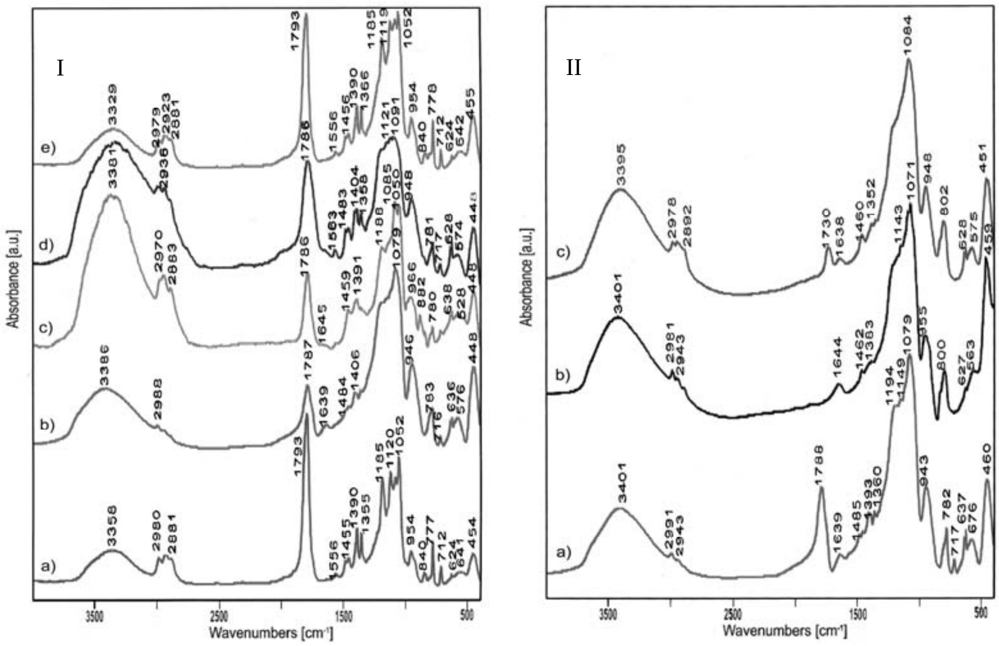

Fig. 3. FTIR spectra of organic-inorganic hybrid gels (heated for 3 hours at 125 °C): T (Ia), S (Ib), Y (Id), Z (Ie); (heated at 80 ˚C for 3 hours): X (Ic), O (II a); and R (II b, heated for 3 hours at 125 ˚C); (IIc-S heated for 5 hours at 210 ˚C). The main components used to obtain the gels and the gel names correspond to those in Table 1

gels obtained, absorption bands originating from Si-O-Si groups are present (the bending vibration of O-Si-O bridges is at about 450 cm^{-1}, the stretching vibration of Si-O-Si bridges at about 1080 cm^{-1}, and the asymmetric stretching vibrations of Si-OH groups at about 950 cm^{-1}).

In the case of the hybrid gels named X, Z and T, the fine structure of the main absorption band, located at about 1050–1100 cm^{-1}, is clearly seen in their FTIR spectra. The observed splitting of this absorption band is probably connected to the vibrations of R_x-Si-O$^-$ bridges. It can be concluded from its absolute intensity and width that the structure of the hybrid gel becomes more ordered in molecular groups in the presence of glycols as organic additives. It also implies less defected bonding states in the molecular groups, although without long distance ordering. The bands originating from the organic parts are found at 2880–2980 cm^{-1} (C–H bonds), 1785 cm^{-1}, and 1185 (C=O, C–O, respectively), and in the range 1330–1480 cm^{-1} (CH_2–O and also likely CH_3 groups). The observed increase in the intensity as well as the shifts in these bands are clearly connected to the addition of glycol species.

Table 3 shows typical results of a porous structure examination for the hybrid materials (S,T) and, for comparison, of silica gels (pure and doped with $LiClO_4$ dissolved in PC, which were heated for 5 hours at 230 °C and 210 °C, respectively), together with results of d.c. conductivity measurements for the S and T hybrid electrolytes.

Table 2. Assignments of the characteristic bands in FTIR spectra [37–41]

Location of IR band about wave numbers, [cm^{-1}]							
Hybrid gels				Silica gels			
T	S	X	Y	Z	O	R	Origin
454	448	448	448	455	450	459	ρ Si–O–Si
541	576	528	574	542	574	563	Li in $LiClO_4$, Li with organics, Si–O ring (4)
624	636	638	628	624	637	628	ClO_4^-, Li–organics (PO)
712	719	716	717	712	717		ν $SiO–C_2H_5$, organics
777	783	780	781	778	782	800	ν_s Si–O–Si, ν_{as} Si–C, ρ_{as} $Si–CH_2$, $Si–O–Si–C_nH_m$
840		882		840			ρ_s $Si–CH_2$
954	946	966	948	954	943	955	ν_{as} Si–OH
1052	1079	1050 1085	1091	1052	1079	1071	ν_{as} Si–O–Si, ν_s Si–O–Si
1120			1121	1119	1149	1143	ν Si–O–R ν Si–O–Si,
1185	1185	1188	1199	1185	overlapped		ν C–C, –OR (C_2H_5), C–O, organics
1355 1390	1406	1391	1358, 1404	1355, 1390	1360, 1408	1383	organics, ν CH_3, ν CH_2 –O
1455	1484	1459	1483	1456	1485	1462	ν C–O–C, organics
1556	1639	1645	1563	1556	1639	1644	H–O–H, molecular
1793	1787	1786	1785	1793	1788		organics, C=O
2881 –2980	2900 –2988	2883 –2970	2800 –2970	2881 –2979	2881 –2979	2943 –2981	ν_{as} CH_2, ν $C–H_x$ of aliphatic organic groups
3358	3360 –3386	3381 (around)	3329 (around)	3340 (around)	3401	3401	ν OH, adsorbed H–O–H, LiOH

Table 3. Results of texture and conductivity examinations

Material	Silica gel pure	Silica gel doped with $LiClO_4$/PC ($x = 0.03$)	*S*	*T*
Single point surface area [m^2/g]	737.77	235.27	1.938	–
BET surface area [m^2/g]	752.69	248.96	3.854	1,881
Langmuir surface area [m^2/g]	1030.1	347.87	2.453	–
Micropore volume [cm^3/g]	0.0943	–0.004	–	–
Micro-pore area [cm^3/g]	219.3	2.6048	–	–
Single point total micro-pore volume, V_{sing} [cm^3/g]	0.3699	0.4177	0.00185	–
BJH adsorption meso-pores volume, V_{meso} [cm^3/g]	0.0928	0.4311	0.00293	–
Average micro-pore diameter (4*V*/*A* by BET) [nm]	1.9657	6.7103	1.9219	–
BJH adsorption average pore diameter [nm]	2.5623	5.6562	4.7708	–
Conductivity σ_{25} [$S\cdot cm^{-1}$]	–	5.6×10^{-5}	1.32×10^{-3}	1.05×10^{-3}

The conductivities of the other hybrid electrolytes, not listed in Table 2, were all of the order 10^{-3} S·cm^{-1}, and specifically 7.26, 6.54, 5.63, 2.14, and 1.39·10^{-3} S·cm^{-1} for samples O, P, X, Y and Z, respectively. The examination of porous structure of hybrid materials containing glycols, especially those of low molecular weight, has proved to be practically aimless due to very low values of BET surface area. In the sol-gel process, the formation of sol particles occurs due to the hydrolysis of alkoxides and subsequent polycondensation of the hydrolysate and gelation of the sol particles. Murakata et al. [42] have investigated the influence of inorganic salts and some surfactants on the pore size distribution in silica gels and have found that the addition of any inorganic salt decreases the gel surface area and depresses the formation of mesopores. Such effects can be considered to be connected with a compression of the dielectric double layer around ions and with a reduction in coagulation stability, which are both effects of the pore size distribution of the gel being altered. They also have observed through SEM examination that the surfaces of gels with low concentrations of inorganic salt, especially those of univalent metals, become flat and smooth, practically without macropores. A similar effect has been obtained with non-ionic surfactants containing alkyl chains, especially PEG additives. Generally, the effect of such additives on the size distribution of the pores in silica gels has been found to be strongly dependent on alkyl chain length. Such results seem to be in good agreement with those obtained in this work from SEM observations and N_2 adsorption measurements for hybrid electrolytes. In addition, polyethylene glycols are known for their hydrophilic properties, and organic low-molecular-weight additives of the hybrid materials obtained in this work can also act as solvents for lithium salts and the other organic components.

The influence of polyethylene glycol (PEG) on the nanostructure of sol-gel derived TiO_2 coatings was studied by Kato and Hiihara [43] with the aim of obtaining nano-sized pores. They established that a temperature as high as 400 °C was not enough to thermally decompose the PEG incorporated into titanium oxide.

In this work, SEM images show smooth and homogeneous surfaces of the samples under examination, and XRD patterns a wide broadening of the background for diffraction angles 2Θ in the range 15–35°, which is characteristic of glassy amorphous materials. In addition, the room temperature conductivities obtained for all the hybrid electrolytes investigated were as high as 10^{-3} S·cm^{-1}. These results can be attributed to suitable conditions, which enable the fast transportation of ionic charge carriers through hybrid electrolytes. Such a condition is a high amorphous phases content, which creates structural paths large enough to accommodate and allow hopping movements of lithium ion, as well as allow for the segmental motion of the polymer chains fragments involved in the structure of the hybrid materials. It is known that polymer electrolytes based on PEO that conduct lithium ions should be in an amorphous state for the effective transport of lithium and counter ions through the polymer. Li^+ is thought to move by a hopping mechanism, which requires a segmental motion of the polymer host. Another model – a free volume model – suggests a correlation of the ionic conductivity of Li^+ with chain segment motion, in which ions move when a local void opens that can accommodate the ion, as is thought to occur in liquids [44].

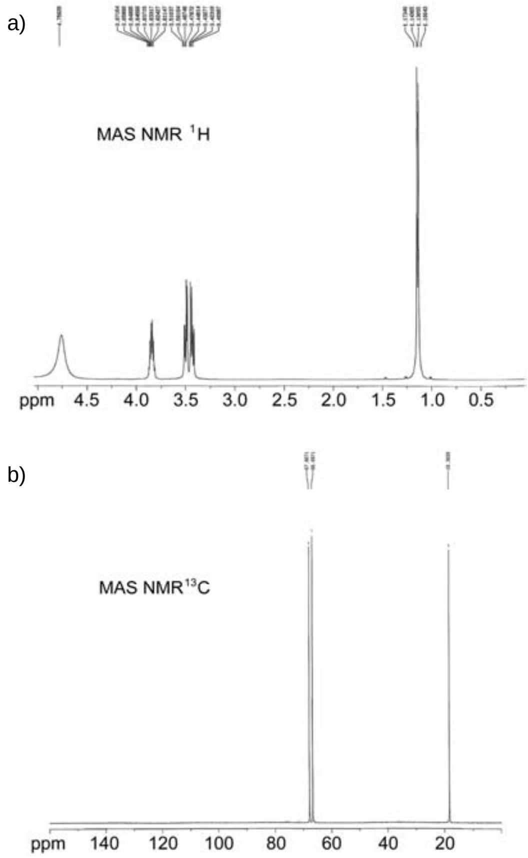

Fig. 4. ^1H (a) and ^{13}C (b) MAS NMR spectra for 1,2-propylene glycol (references for NMR measurements of the hybrid electrolytes O and X)

The addition of propylene carbonate and some other low molecular weight organic compounds to the PEO improves ionic transport by reducing the glass transition temperature of the polymer [7, 45, 46]. Ito et al. [45] have studied the influence of low -molecular-weight glycols on the ionic conductivity of the PEO–$LiCF_3SO_3$ complex electrolyte and have established that the conductivity increases with the decreasing molecular weight of PEG and with increasing PEG content. Significant conductivity enhancement at room temperature can be attributed to an increase in the content of amorphous regions, which are responsible for ionic conduction. In alkali ion -conducting glasses, mobile ion conduction is also thought to proceed by means of free volume, i.e. voids, and at a given alkali content the ionic conductivity can be enhanced by increasing the free volume. Nevertheless, ionic conductivity is first of all dependent on the number of mobile ions and on the ion–ion distance in conduction paths. The structural changes in silica bonding states due to organic additions and doping with lithium were expected to change the coordination of oxygen atoms, result in the partial dissociation of immobile species from non-bridging oxygen atoms, and enlarge the pathways available for migration of lithium ions in the frame of the silica host [47]. The characteristic structural properties of the hybrid materials obtained in this work, as revealed by infrared spectroscopy, can be considered to correspond well with such assumptions.

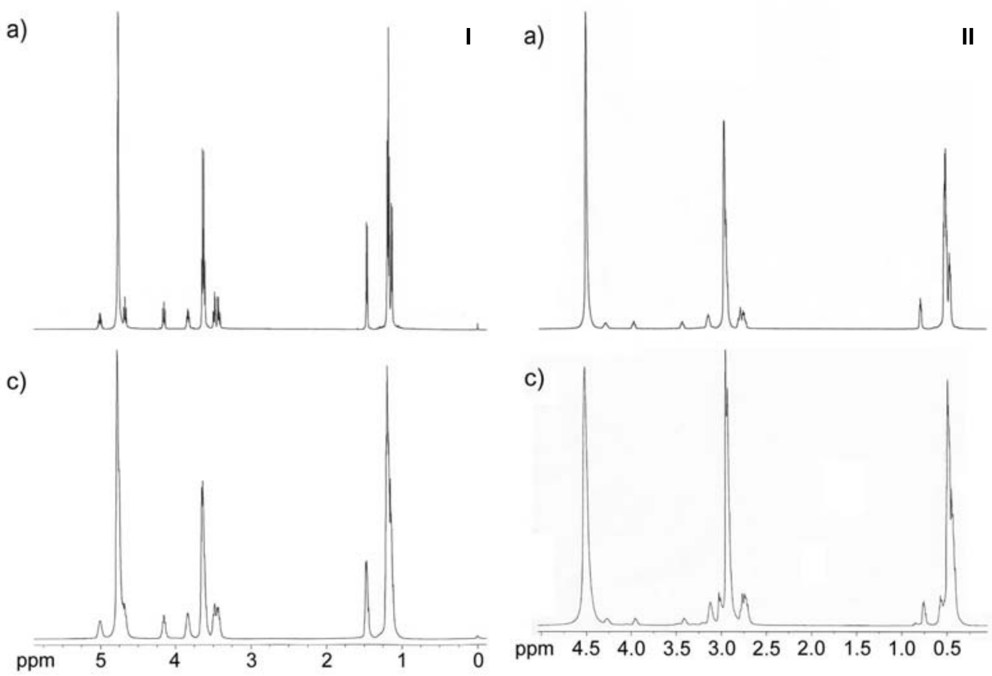

Fig. 5. ^{1}H MAS NMR spectra for hybrid materials: O (I, stages a and c) and X (II, stages a and c)

The sharp diminishing of porous structures, which are significantly developed and clearly connected with the silica gel parts in hybrid materials containing other additives (PEO, PO), is especially pronounced for the O and X hybrid materials (which have low-molecular-weight glycols as organic additives). Samples of these two materials were examined additionally by MAS NMR (^{13}C, ^{1}H) spectroscopy. The NMR spectra of samples of each material were recorded three times with a waiting time of about a week between each observation. The first time spectra were taken two days after the reaction of hydrolysis in the sols, and the following spectra were recorded 7 and 14 days later. The final MMR measurements were conducted a few hours before the complete sol to gel transformation had occurred. The NMR spectra of the hybrid materials O and X were referenced to those recorded for 1,2- propylene glycol.

The ^1H and ^{13}C NMR spectra for 1,2-propylene glycol are shown in Figs. 4a, b, respectively, and the spectra for the hybrid electrolytes O and X are given in Figs. 5–7.

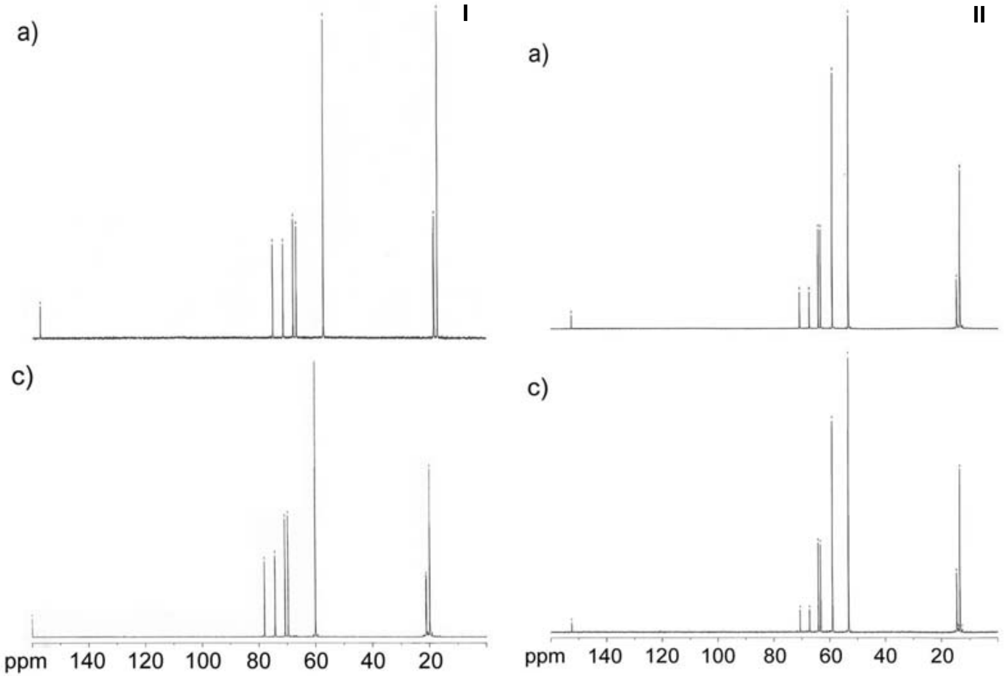

Fig. 6. ^{13}C MAS NMR spectra for hybrid materials: O (I, stages a and c) and X (II, stages a and c)

No ^1H or ^{13}C MAS NMR spectra of hybrid gels obtained from mixtures of similar components to those under investigation here have been previously reported in the available literature. The chemical shifts and intensity changes of the signals originating from the starting components of the sols, as well as the appearance of new bands and disappearance of D_2O bands, which was used as a solvent for the O samples, can be ascribed to structural reordering due to the formation of the hybrid cross-linked structure between the organic and inorganic parts of the materials under investigation. In the spectra registered during the first two stages of the gelation process, only relatively small differences were observed, mainly intensity changes, which indicate that low-molecular-weight glycol species delay the waiting time for the resulting structural order, perhaps due to the cage effect. An example in which such an effect occurs has been described by Matějka et al. [48], where the sol-gel polymerisation of a hybrid material resulted in the growth of a polysilsesquioxane structure when glycidyloxypropyltrimethoxysilane was used. On the other hand, the reactivity of the O material, containing 1,2-propylene glycol and PC as organic additives, has proved to be high enough to incorporate all the D_2O applied as a solvent in the preparation of the sample for final NMR measurements (Fig. 7). In the region of silanol signals (dominated at 3.83–3.41 ppm, Fig. 7), there is a significant split, decrease in intensity, as well as a chemical shift in signal localization, which is clearly connected with a cross-linked bonding process that develops between the organic and inorganic parts of the starting sols [49]. NMR studies of the hybrids synthesized in this work, among others, will be continued with the aim to explain the vanishing of porous structures (or capturing).

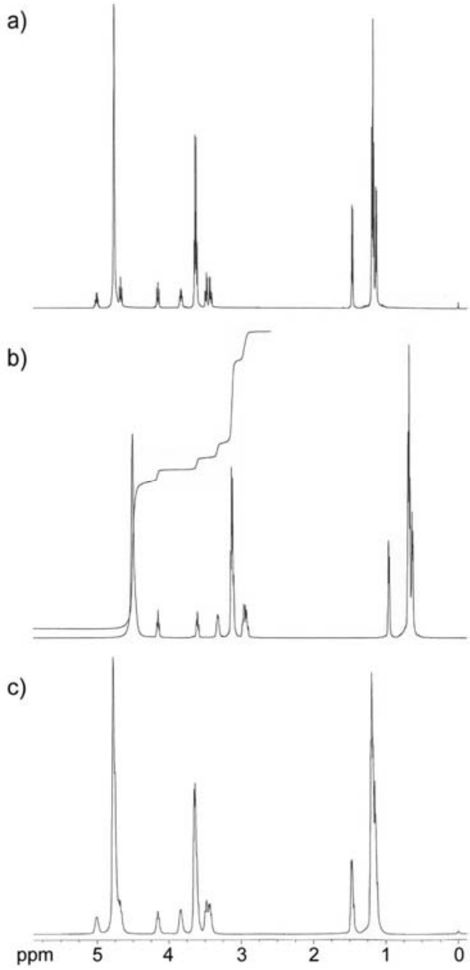

Fig. 7. ^{1}H MAS NMR spectra for the hybrid material O (stages a–c)

The organic-inorganic hybrid materials obtained in this work were examined as electrolytes for cells based on the WO_3 thin film with an electrochromic window arrangement. A typical response to a rectangular shaped current signal and a cyclic voltammogram (CV) taken for the electrochromic cell under (±) polarized low d.c. voltage are shown in Fig. 8 (a, b), respectively. The transmission photometric characteristics of WO_3-based electrochromic systems with a NiO film as the counter-electrode material are given in Fig. 9.

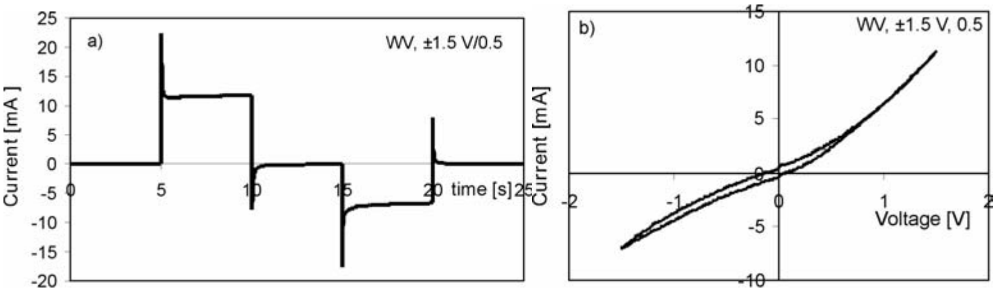

Fig. 8. Current response (a, plane line) and cyclic voltammogram (b, dashed line) for thin film tungsten oxide/organic-inorganic hybrid electrolyte Y (TEOS, PEG (6000)/H_2O, $LiClO_4$/PC/0.02)/vanadium oxide electrochromic cell, cycled with a voltage of ± 1.5 V (cycled area 3 cm^2, scan rate 50 mV/s)

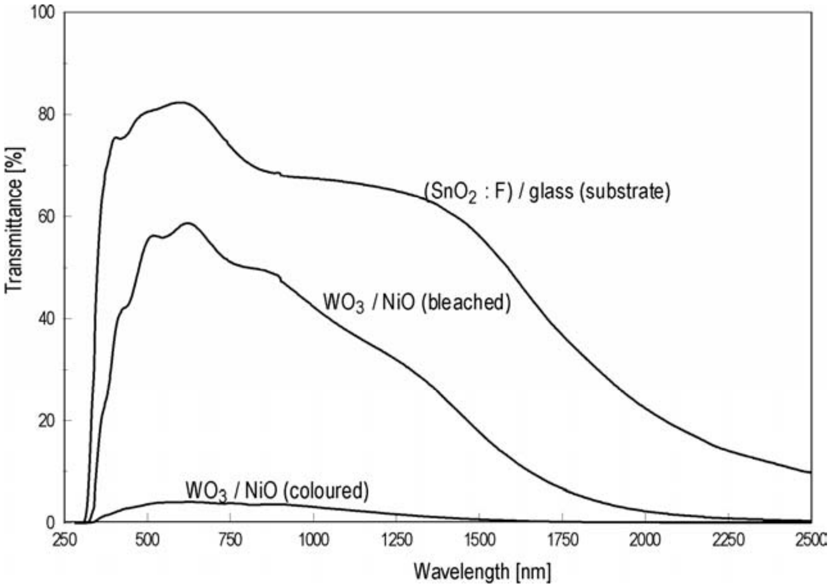

Fig. 9. Typical transmission characteristics as a function of the wavelength for a thin metal oxide electrochromic coating system: WO_3 /organic –inorganic hybrid electrolyte Z (TEOS, PEO-PEG (15000)/CH_2Cl_2, 1,2-PG, LiCl /H_2O/0.02)/ NiO, with electrochromic metal oxide materials coated by spray pyrolysis onto a glass substrate with (SnO_2 :F) layers, (presented in the coloured and bleached states, with lithium ions inserted/extracted into the WO_3 structure under a d.c. voltage range of (±) 2.5 V)

All the sol-gel derived hybrid materials obtained in this work were able to take part in electrochromic reactions, which depend on the insertion/extraction of lithium ions and injection/extraction of electrons, and which result in reversible dark blue or colourless states of the tungsten oxide layer. The d.c. conductivity values for the hybrid electrolytes under investigation were of the order of magnitude 10^{-3} $S\cdot cm^{-1}$ when measured at room temperature. They have proved to be dependent on composition and morphological properties, and connected with structural modifications due to organic additives. The values of ionic conductivity reported there, are improved by about one order of magnitude in comparison to those obtained by the authors previously for electrolytes of mixed silica–PEO systems (with and without chemical bonds between the organic and inorganic parts) [50], and similarly in comparison to the results reported by Dahmouche et al. [32] for hybrid electrolytes of silica–PEG_{300} systems doped with lithium salt and without chemical bonds between the organic and inorganic phases. Generally, the ionic conductivity of sol-gel derived hybrid electrolytes is higher for those that are lithium ion and/or proton conductors [29]. The conductivity values of hybrid electrolytes obtained in this work with lithium salt doping are about two to three orders of magnitude higher than those described by Chaker et al. [35] for siloxane–PPO hybrid ormolytes doped with sodium perchlorate.

4. Summary

Sol-gel derived, lithium ion conducting, amorphous, organic-inorganic hybrid materials, containing about 20% of organic additives, were obtained from TEOS, PEO, PO, PC, PEG, EG, and 1,2-PG with the aim to be used as solid electrolytes for electrochemical and optoelectronic applications.

All of the synthesized hybrid materials have proved to be amorphous and homogeneous, with morphology and textural properties significantly differing between each other, corresponding with the variety of compositions of the starting solutions. They were all stable at temperatures as high as 125 °C.

The organic-inorganic hybrid character of the gels obtained in this work has been confirmed by the results of infrared spectroscopy investigations.

All the hybrid sol-gel derived materials obtained have proved to be suitable as transparent and colourless lithium ion conducting electrolytes when examined in electrochemical cells with a thin film electrochromic window arrangement based on WO_3, with a d.c. conductivity of the order of 10^{-3} $S\cdot cm^{-1}$.

Additional studies are required and will be carried out with the aim of explaining the suppression of porous structures, as measured by nitrogen adsorption in hybrid materials with low molecular weight glycols as organic additives. The reason for this phenomenon, which is most intensively observed for the O and X hybrid materials, seems to be caused by liquid phase addition due to the cage effect and/or trapping.

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