

Organic–inorganic hybrid materials doped with lithium ions

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Organic–inorganic hybrid materials have been synthesized by the sol–gel method, using tetraethyl orthosilicate (TEOS), poly(ethylene oxide) (PEO), net-polyacrylic-*inter-net*-polysiloxane, butyl acrylate, ethyl acetoacetate, tetrahydrofuran, acetonitrile and LiClO₄ precursors and additives. Mass fractions of the organic additions in the gels were of *ca* 35–40 mass%. The hybrid materials obtained were amorphous, colourless, transparent or translucent, with room temperature ionic conductivities in a range of 10⁻⁴–10⁻³ Ω⁻¹cm⁻¹. The results of scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM/EDX), Fourier transform infrared spectroscopy and ²⁹Si MAS Nuclear Magnetic Resonance analysis have revealed [SiO₄] tetrahedrons polycondensation strongly influenced by organic precursors and chemical bonding between organic and inorganic parts of the gels obtained.

Keywords: organic–inorganic hybrids, lithium-ion conductivity, sol–gel.

1. Introduction

In the last years, there has been observed intensive development in employing of the sol–gel method and procedures for preparing hybrid organic–inorganic materials, especially organically modified silanes (ormosils) [1, 2]. The sol–gel synthesis starting from the solution of the precursors at low temperatures makes it possible to obtain new materials with various interesting properties due to appropriate additives introduced into sols, including dyes, ultra fine particles, polymers and rare earth metal compounds [3–6]. Amorphous organic–inorganic hybrid materials have recently attracted a great attention of researchers for integrated optical and solid

electrolyte applications [7, 8]. Sol–gel derived hybrids with ionic conductivities of at least 10^{-4} – 10^{-3} S·cm⁻¹ at ambient temperatures have the potential of applications in solid-state rechargeable batteries, sensors, electrochromic displays and advanced windows [9–14]. Though there are reports [1, 2, 15–17] on hybrid organic–inorganic materials doped with alkali metal ions or protons with the aim to obtain solid electrolytes, the modifying effect of such a doping and organic additives introduced into sols on structural properties and ionic conductivity of the gels based on TEOS, has still remained insufficient.

In this work, organic–inorganic hybrid electrolytes have been synthesized from tetraethyl orthosilicate TEOS, butyl acrylate, net-polyacrylic-*inter-net*-polysiloxane, poly(ethylene oxide) PEO, ethyl acetoacetate, tetrahydrofuran (butylene oxide), propylene carbonate (PC), dichloromethane, acetonitrile, ethanol and butanol precursors and solvents. Lithium perchlorate dissolved in PC has been employed as a salt for doping at a weight ratio of about 0.01 with respect to the mass of the fresh gels. The hybrid materials obtained were investigated for morphology, structural properties and ionic conductivity with the aim to determine the effect of the organic additives and potential of the hybrids obtained to be useful as transparent solid electrolytes for the room-temperature applications.

2. Experimental

Silica component of the organic–inorganic hybrids and lithium ions doped silica gel, prepared as a reference for comparison, were produced by mixing TEOS (Si(OC₂H₅)₄) and distilled water with the molar ratio of TEOS:H₂O = 1 : 4. As a catalyst, 36.6% HCl was added drop by drop up to pH = 2. Organic parts were produced from butyl acrylate (BA, C₇H₁₂O₂), net-polyacrylic-*inter-net*-polysiloxane (nPA-PS, polymer of butyl acrylate, allyl, methyl and 3-(dimethoxymethylsilyl)propyl methacrylates interpenetrated with cyclic dimethylsiloxanes; (this substance is not yet fully tested at present), PEO, [-(CH₂CH₂O)_n]-, $M \approx 600.000$], ethyl acetoacetate (EAA, C₆H₁₀O₃), propylene carbonate (PC, C₄H₇O₃), tetrahydrofuran (THF, butylene oxide; diethylene oxide; oxacyclopentane, C₄H₈O), dichloromethane (CH₂Cl₂), ethanol (C₂H₅OH), butanol (C₄H₉OH) and acetonitrile (CH₃CN), precursors and solvents. As a salt for doping at a weight ratio of about 0.01 with respect to the mass of fresh gels, LiClO₄ dissolved in PC or ethanol was applied. Components (at least of reagent grade, Merck and Aldrich) employed for preparing gels are listed in Tab. 1.

Mass fractions of the organic precursors were calculated on *ca* 30 or 40 mass%, at the weight concentration of nPA-PS:PEO (or PEO) equal to 1 and EAA:BA ratio ranged from 0.2 to 0.8. Solutions of TEOS, after stirring for 1 hour, were mixed with solutions of organic compounds in appropriate solvents (dichloromethane, tetrahydrofuran, acetonitrile, ethanol and/or butanol). The resulting mixtures were stirred for 3 hours. Gelation process occurred within several hours to 1.5 days. Fresh gels were aged for three weeks at ambient temperature and then dried for 3 hours in an electric drier at 80 °C.

Table 1. Components of starting solutions.

Sample	Components	Appearance, remarks
E	TEOS (sol), ethanol, LiClO ₄	colourless, transparent
P-0	TEOS (sol), PC, LiClO ₄	colourless, transparent
P-1	TEOS (sol), THF, PC, LiClO ₄	colourless, transparent
P-2	TEOS (sol), nPA-PS, BA, THF, PC, CH ₃ CN, CH ₂ Cl ₂ , LiClO ₄	colourless, transparent
P-3	TEOS (sol), nPA-PS, BA, EAA, THF, CH ₃ CN, PC, CH ₂ Cl ₂ , LiClO ₄	colourless, slightly opalescent
P-4	TEOS (sol), nPA-PS, PEO, BA, EAA, PC, CH ₂ Cl ₂ , ethanol, LiClO ₄	colourless, transparent
P-5	TEOS (sol), BA, PEO, nPA-PS, PC, butanol, ethanol, CH ₂ Cl ₂ , LiClO ₄ ; (nPA-PS:PEO \approx 0.1)	colourless, slightly opalescent
P-6	TEOS (sol), BA, EAA, PC, LiClO ₄	colourless, transparent
P-7	TEOS (sol), PEO, BA, PC, CH ₂ Cl ₂ , LiClO ₄	colourless, transparent

The morphology and structural properties of the hybrid materials and silica gel as a reference for comparison, synthesized in this work, were examined by scanning electron microscopy equipped with energy dispersive X-ray spectroscopy SEM/EDX, (JEOL JSM 5400 with LINK An 10/5, NOVA NANOSEM – FEI), Fourier-Transform Infrared Spectroscopy (Bio-Rad FTS-60VM FTIR spectrometer, KBr technique) and Nuclear Magnetic Resonance ²⁹Si MAS NMR (NMR spectrometer at the magnetic field 7.05 T). A.c. conductivity was measured with RCL-meter (HIOKI 3532-50 RCL HiTESTER). The spectral characteristics at \pm polarized d.c. potential applied to the thin film electrochromic cell based on WO₃ (*ca* 120 nm thick) and NiO (*ca* 160 nm thick) active electrode and counter-electrode, respectively, were registered with UV-VIS-570 Jasco spectrophotometer. Thin electrochromic films were coated onto the low-emissivity glass (K-Glass, Pilkington) by the pyrolysis method at temperatures ranging from 600 to 680 °C, using solutions of metal acetylacetonates as coating precursors. The procedures used to obtain thin metal oxide films were the same as those previously described [18].

3. Results and discussion

The appearance of gels after heat treatment is described in Tab. 1. All the gels obtained have revealed an amorphous structure under XRD examination (patterns not presented there because of a paper length limitation). Figure 1 shows typical SEM images (surface view or fractured surface, at magnification of 50 000 \times).

When examined by using SEM/EDX, the morphology of the samples turned out to be homogeneous with the elemental analyses results corresponding to the components of the sols. The SEM/EDX examination has revealed homogeneous fine and smooth surface morphologies of all the hybrids obtained in this work, while there in the fractured surface images of samples P-2, P-3 and P-4 containing large

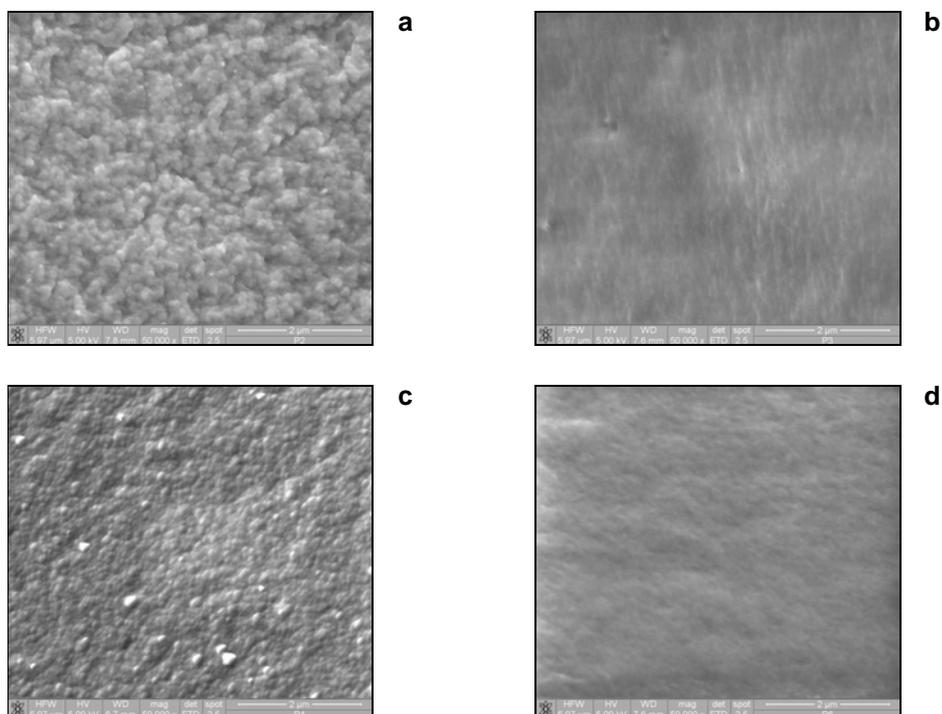


Fig. 1. SEM images of hybrids at a magnification of 50000 \times : P-2 (a), P-3 (b), P-4 (c), P-1 (d); b, d – surface view; a, c – fractured surface.

amounts of nPA-PS together with BA (P-2, P-3) and additionally with PEO (P-4), the micron-sized particles linked into the chains with the voids between them can be observed at the high magnifications.

FTIR spectra of the gels under investigation, heated at 80 °C, are shown in Fig. 2. ^{29}Si NMR spectra and calculated results of the gel materials synthesized in this work are given in Fig. 3 and Tab. 2, respectively.

^{29}Si MAS NMR spectra and calculated results (Fig. 3 and Tab. 2, respectively) of the hybrid electrolytes and lithium doped silica gel (E) given for comparison, exhibit peak profiles with different amounts of the Q_4 , Q_3 and Q_2 structural units, corresponding to the silicon Si in coordination 4, 3 or 2 in respect to the bridging oxygen atoms. The analysis of these spectra was based on the numerical values of the parameter A_1 equal to the ratio of Q_4/Q_3 and parameter A_2 equal to the ratio of Q_4/Q_2 calculated from the relative fractions of the peak area, corresponding to the appropriate Q species, where Q_4 value at approximately -109 ppm corresponds to $[\text{SiO}_4]$ tetrahedrons. The observed chemical shifts were referenced to the signal of tetramethyl silane (TMS).

A.c. measurements of the ionic conductivities at room temperature for the gel materials obtained have revealed values σ_{25} in a range of 10^{-4} – 10^{-3} $\text{S}\cdot\text{cm}^{-1}$ for all

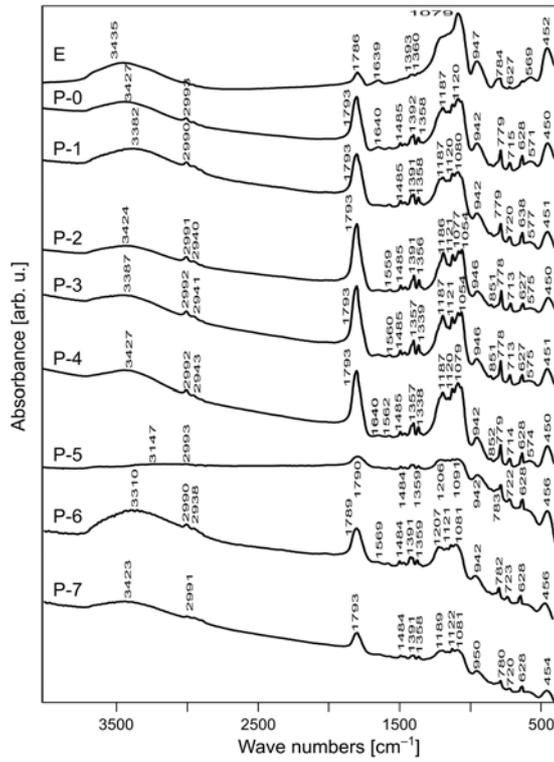


Fig. 2. FTIR spectra of hybrid gels heated for 3 h at 80 °C.

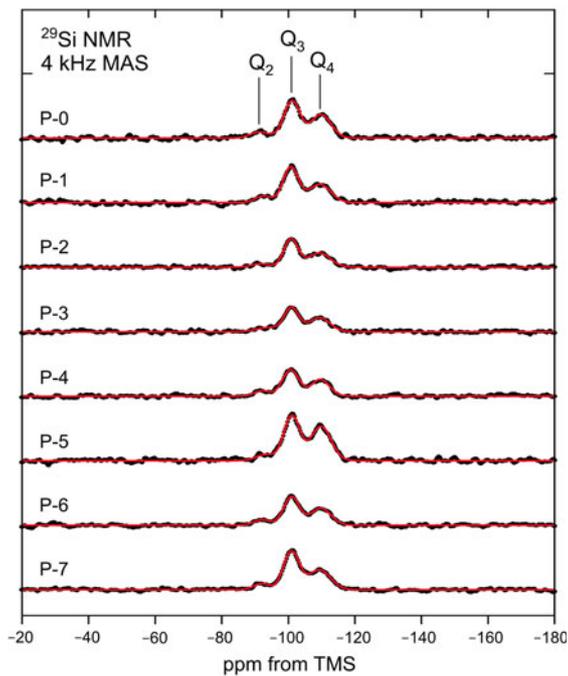


Fig. 3. ²⁹Si MAS NMR spectra for hybrid gels P-0–P-7.

T a b l e 2. Isotropic chemical shifts (δ , ppm), line widths (half width at half maximum: hwhm, ppm) and relative fraction (%) of Q_n units in hybrid materials and silica gel E.

Sample	Q_2			Q_3			Q_4		
	$-\delta$, hwhm [ppm]; relative share [%]			$-\delta$, hwhm [ppm]; relative share [%]			$-\delta$, hwhm [ppm]; relative share [%]		
E	-92.2 (5.5) 7			-101.0 (7.2) 51			-109.9 (7.2) 42		$A_1 = 0.82$ $A_2 = 6.00$
P-0	-91.0 (6.8) 9			-100.8 (5.7) 51			-109.5 (7.1) 40		0.78 4.44
P-1	-92.1 (5.6) 10			-100.4 (5.5) 52			-109.1 (7.7) 38		0.73 3.80
P-2	-91.4 (6.3) 7			-100.5 (5.0) 52			-108.9 (7.8) 41		0.79 5.86
P-3	-93.8 (8.8) 14			-100.6 (5.1) 46			-109.0 (7.4) 40		0.87 2.86
P-4	-91.4 (5.4) 10			-100.4 (5.9) 53			-109.3 (6.4) 37		0.70 3.70
P-5	-92.8 (6.7) 7			-100.7 (5.7) 47			-109.5 (7.2) 46		0.98 6.57
P-6	-91.7 (6.0) 10			-100.6 (5.6) 51			-109.4 (7.2) 39		0.76 3.90
P-7	-91.7 (5.7) 8			-100.6 (5.6) 53			-109.0 (7.8) 39		0.74 4.88

the hybrids, and of $10^{-5} \text{ S}\cdot\text{cm}^{-1}$ for gel E. The measured values of the ionic conductivity σ_{25} (in $\text{S}\cdot\text{cm}^{-1}$) at lithium salt doping of 0.01 mass% in respect to the mass of the fresh gels, were $4.32\cdot 10^{-5}$, $1.22\cdot 10^{-4}$, $2.46\cdot 10^{-4}$, $7.26\cdot 10^{-4}$, $5.07\cdot 10^{-4}$, $2.75\cdot 10^{-3}$, $2.07\cdot 10^{-3}$, $8.32\cdot 10^{-4}$, $1.23\cdot 10^{-3}$, for samples E, P-0, P-1, P-2, P-3, P-4, P-5, P-6, and P-7, respectively, at the $\pm 0.08\%$ basic accuracy of the measurement. The best values ($2.75\cdot 10^{-3}$ and $2.07\cdot 10^{-3} \text{ S}\cdot\text{cm}^{-1}$) were obtained for hybrid gels P-4 and P-5, respectively, with complex compositions and additives of BA, PEO, and nPA-PS.

All the organic–inorganic hybrid materials obtained in this work were examined as electrolytes for WO_3 based thin film cells with an electrochromic window arrangement. A typical spectral transmittance characteristics registered for the electrochromic cell under (\pm) polarized low d.c. voltage, using hybrid P-4 as an electrolyte, are shown in Fig. 4.

The SEM/EDX examination of the hybrids containing acrylates has revealed micron-sized particles connected into some of chains with the voids between them, which can be observed in the fractured surfaces at high magnifications. This phenomenon, observed especially in the hybrids P-2–P-4, containing butyl acrylate, large amounts of nPA-PS as well as PEO and/or EAA, seems to be connected with cross-linking polymerization, most likely due to bonding of inorganic and inorganic parts by means of carboxylic and hydroxyl groups present in acrylates. The carboxylic groups of the acrylic acid derivatives have been reported as crosslinkers of the polymer particles and hybrid organic–inorganic systems, by LEE *et al.* [19] and ZHOU *et al.* [20], respectively. In that case, the growth of particles can be ascribed to crosslinking of the polymer and silica particles by means of carboxylic groups, connected with capturing of monomers, nuclei and/or oligomeric radicals from the system during the polycondensation process. Hence, the dispersion polymerization observed in hybrids under investigation can be ascribed to the condensation of silica particles from the hydrolysis and polymerization reactions of TEOS, overlapped with crosslinking activity of the carboxylic and OH^- groups. The presence of such groups

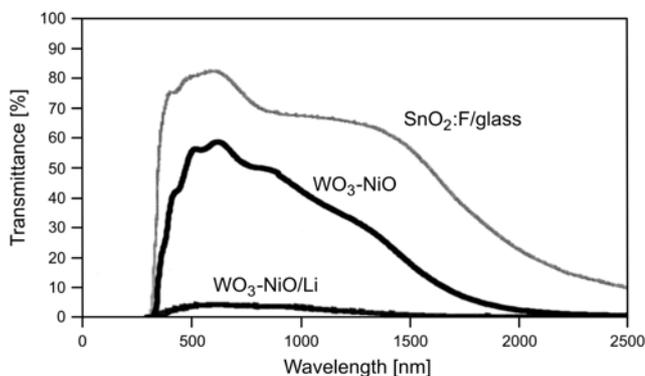


Fig. 4. Typical spectral transmittance characteristics for $\text{WO}_3\text{-NiO}$ thin film coatings of an electrochromic window arrangement, coloured and bleached under ± 1.5 V polarized d.c. voltage, with hybrid P-4 employed as electrolyte.

in the hybrids containing acrylic acid derivatives is confirmed by the results of FTIR spectroscopy.

The results of the FTIR analysis (Fig. 2) are given for gels heated at 80°C . The absorption bands characteristic of water (H-O-H at around 1638 cm^{-1} and OH^- in H_2O at around $3375\text{--}3443\text{ cm}^{-1}$) and of the Si-O-Si bonds, assigned to Si-O-Si asymmetric stretching in a range of $1000\text{--}1100\text{ cm}^{-1}$, Si-OH asymmetric stretching at around $942\text{--}946\text{ cm}^{-1}$, Si-O-Si symmetric stretching at around 800 cm^{-1} and bending vibration of the Si-O-Si groups at around 450 cm^{-1} , were found in the FTIR spectra of all the gels under investigation [15, 21, 22]. All the spectra of organically modified gels exhibit absorption bands characteristic of organic parts and organic–inorganic bonds. Specific regions of the FTIR spectra in which absorption bands are observed, correspond to signals of: Si-CH_2 , $-\text{O-Si-C}_n\text{H}_m$; Si-O-R , C-O ; organic parts, C-H in C_nH_m , C-O-C , $-\text{CO(OH)}^-$; Si-CO(OH) , CH_3 , CH_2 ; organic parts, C=O ; organic parts, C-H , CH_2 ; C-H , at around ($778\text{--}852$; $1110\text{--}1189$, $1206(7)$; $1338\text{--}1485$; $1558\text{--}1569$; $1786\text{--}1793$; $2938\text{--}2993$; 3147) cm^{-1} , respectively. The amount, position and intensity of the bands from organics, which seem to be evidently connected with organic additives, have been employed [18–25]. Bands at around 570 cm^{-1} from the absorption of lithium in LiClO_4 and bonded to organics are observed in the FTIR spectra of all the hybrid electrolytes obtained. Additionally, besides lithium bonded to organics, the peaks from ClO_4^- at about 628 cm^{-1} can be observed, indicating the presence of free lithium salt ions.

The distinct splitting of the main absorption band (originated from Si-O vibration and localized at about 1100 cm^{-1}) showing the presence of broken oxygen bridges, is clearly seen in the spectra of hybrids P-1–P-4, but in a relatively weak form occurs in hybrids P-6 and P-7 and nearly vanishes in the spectrum of gel P-5. Moreover, similar correlation can be observed in the intensity of bands related to organic parts ($1356\text{--}1485\text{ cm}^{-1}$) and C=O double bond (at about 1793 cm^{-1}),

indicating that gels P-1–P-4 have inorganic polycondensation process less developed than the remaining hybrids under investigation and overlapped in a significant degree by the organic–inorganic cross-linking process, probably connected with a cage effect in case of the hybrid P-5 with a C–H bonding at about 3147 cm^{-1} [15].

The results of ^{29}Si MAS NMR spectroscopy are based on the numerical values of the parameter A_1 equal to the ratio of Q_4/Q_3 and the parameter A_2 equal to the ratio of Q_4/Q_2 species (Tab. 2). The higher A_1 and A_2 values, the higher is a polycondensation degree of the silicon-oxygen network. The NMR measurements with a good agreement with the results of SEM/EDX and FTIR, indicated the less developed polycondensation of the inorganic network for hybrids P-1, P-3, P-6 and P-7, with a relatively large content of low molecular weight organic additives, and considerably more advanced and likely overlapped with cross-linking the polymerization and trapping effect in the gels P-2 and especially P-5.

4. Conclusions

Sol–gel derived, lithium-conducting, organic–inorganic hybrid gel materials have been synthesized from tetraethyl orthosilicate TEOS, butyl acrylate, net-polyacrylic-*inter-net*-polysiloxan, poly(ethylene oxide) PEO, ethyl acetoacetate, tetrahydrofuran (butylene oxide), propylene carbonate (PC), dichloromethane, acetonitrile, ethanol and butanol precursors and solvents. The hybrid structure of the gels has been revealed by FTIR and ^{29}Si NMR investigation. The $[\text{SiO}_4]$ tetrahedrons polycondensation seems to be associated with cross linking process likely due to carboxylic groups from acrylic acid derivatives used as organic additives of the hybrids. Relatively large room-temperature ionic conductivity, of about 10^{-4} – $10^{-3}\text{ S}\cdot\text{cm}^{-1}$, can be attributed to amorphous character and organic modifications resulting in the development of structures more accessible for lithium ions migration. All the hybrids obtained have proved to be electrochemically effective in reversible electrochromic reactions, which makes them be prospective as electrolytes for ambient temperature electrochemical and optoelectronic applications. With the aim to determine exactly a structure and conductance mechanism correlations in lithium ion doped hybrid materials prepared in this work, further investigations have been undertaken.

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