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Li-ion conducting organic–inorganic hybrid electrolytes

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Lithium ion conducting, sol-gel derived, amorphous, organic–inorganic hybrid electrolytes were obtained from tetraethoxysilane, poly(ethylene oxide), propylene oxide, propylene carbonate, acetonitrile and $LiClO_4$ precursors, and were investigated for their morphological and structural properties by scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM/EDX), X-ray diffraction (XRD), infrared spectroscopy, and nitrogen adsorption at 77 K. A room-temperature conductivity of *ca.* 10^{-4}–10^{-3} $S\cdot cm^{-1}$, attributed to an amorphous character and the organic addition, as well as results of testing in WO_3–based electrochromic thin-film systems, make the hybrid materials obtained promising as electrolytes for ambient temperature electrochemical and optoelectronic applications.

Key words: *organic-inorganic hybrid; sol-gel; solid ionic electrolyte; electrochromic coating*

1. Introduction

Solid materials with high ionic conductivities at ambient temperatures have attracted much attention in recent years, because of their possible application as electrolytes in advanced optoelectronic and electrochemical devices, such as rechargeable lithium batteries, and electrochromic windows and displays [1-3]. Electrolytes for applications in electrochromic windows are additionally required to be colourless and transparent. Polymer electrolytes at ambient temperatures have large contents of crystalline regions, causing a decrease in ionic conductivity [3-7]. On the other hand, due to the process starting from solutions of precursors prepared at room temperature, the sol-gel route has been successfully employed for producing amorphous transparent

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materials, including organically modified gels [8–10]. Among others, Park and Nagai [10] have reported on sol-gel derived organic-inorganic hybrid proton-exchange membranes for fuel cells application.

In this work, sol-gel derived, lithium ion conductive organic-inorganic hybrid electrolytes were synthesized and investigated by scanning electron microscopy equipped with energy dispersive X-ray spectroscopy SEM/EDX, X-ray diffraction (XRD), infrared spectroscopy (FTIR) and nitrogen adsorption at 77 K. D.c. conductivity was measured using a four-electrode cell. Photometric and current–voltage characteristics were observed in WO_3 - based thin film electrochromic systems, at (±) polarized dc potential applied through a potentiostat/galvanostat.

2. Experimental

Silica components of organic- inorganic hybrids, and silica gels prepared for comparison, were produced from TEOS [$Si(OC_2H_5)_4$] and distilled water with the molar ratio of TEOS : H_2O = 1 : 4. As a catalyst, 36.6 % HCl was added, up to pH = 2. Organic parts were prepared from PEO, $–(CH_2\ CH_2O)_n–$ ($M_w \approx 600\,000$), propylene oxide (PO, C_3H_6O, $M_w = 58.08$), propylene carbonate (PC, C_4H_6O), dichloromethane (CH_2Cl_2), ethanol (C_2H_5OH) and acetonitrile (CH_3CN) (Table 1). As a salt for doping at weight ratio of about 0.02 and 0.03 with respect to the mass of fresh gels, $LiClO_4$ dissolved in PC or water (sample C) was employed. Solutions of TEOS, after stirring for 1 hour, were mixed with solution of PEO and/or PO and PC, and the resulting mixtures were stirred for 3–3.5 hours, up to the end of hydrolysis reaction. Mass fractions of organic additives were of *ca.* 20 mass% in gels, with a weight ratio of PEO: PO and/or PC equal to 1, and molar ratio of PO: PC equal to 1.

Table 1. Components of starting solutions for gels under investigation

Sample	Components	$LiClO_4$ weight fraction	Appearance, remarks
A	TEOS, PC	0.02	organic glass, colourless, transparent
B	TEOS, PEO/CH_2Cl_2, PC	0.03	
C	TEOS, PEO/CH_3CN	0.02	
K	TEOS, PEO/CH_3CN, PC	0.02	
D	TEOS, PO, PC	0.02	organic glass, slightly opalescent
F	TEOS	0.03	transparent silica glass

Fresh gels were stored for two weeks with a small surplus of ethanol and/or dichloromethane and then dried for a week at ambient temperature and for 3–5 h at temperatures of 80–230 °C. The hybrid gels to be used as electrolytes were spread onto glass sheets with thin films of: (SnO_2:F) and WO_3, and V_2O_5 and CeO_2/TiO_2, respectively, prepared by pyrolysis method, as was described earlier [11].

3. Results and discussion

The duration of sol-gel transformation ranged from several minutes for gel D to 1.5, 2, 3, 2–4 and 6 days, respectively for gels A, B, C, K, and pure or lithium doped silica gels. Hybrid gels remained transparent after 3-hour heating at temperatures 125–150 ºC and XRD patterns of all the gels obtained were typical of amorphous materials. SEM images of hybrid gels are shown in Figures 1a–d. FTIR spectra for hybrid gels B, C, D, K are shown in Figure 2. Assignments of the characteristic absorption bands in infrared are listed in Table 2.

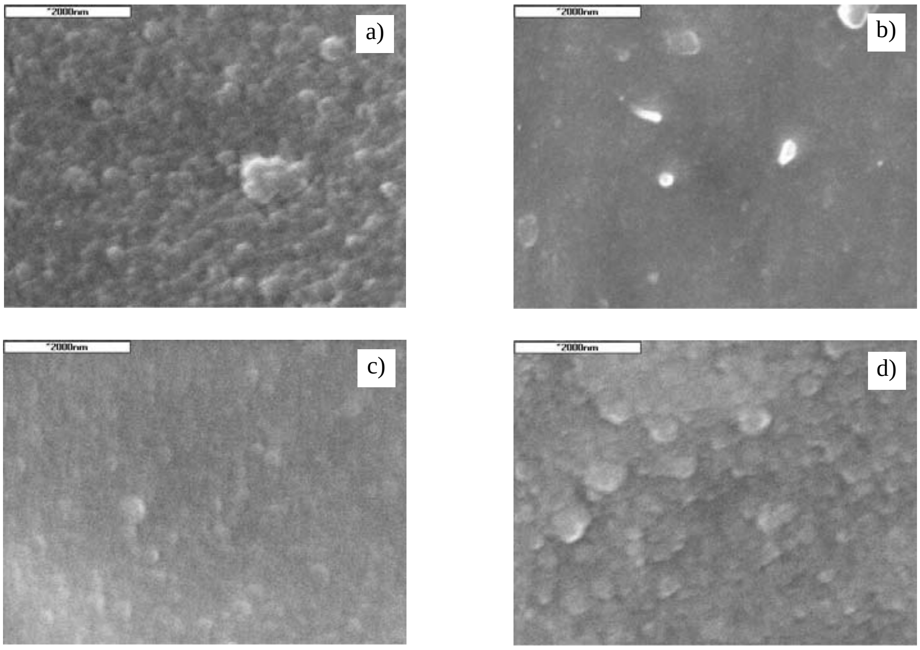

Fig. 1. SEM images (at magnification of 20 000×, the bar corresponds to 2000 nm) for samples of the hybrid gels heated at 125 ºC: a) gel C, b) gel K, c) gel D, d) gel B

In FTIR spectra of gels under investigation (Fig. 2), there can be seen absorption bands characteristic of water in molecular and adsorbed forms (ca. 3400 and 1620 cm^{-1}, respectively). Lithium incorporation into gel structures, resulting in breaking of the oxygen bridges, appears in splitting of the main absorption band, localized at ca. 1080 cm^{-1}. The absorption band at ca. 782 cm^{-1} is characteristic of the hybrid gels only. According to Gunzler and Gremlich [12], it can be ascribed to vibrations of O–Si–C_nH_m species, providing the evidence of formation of the hybrid structure in gels with organic additions, in which the organic and inorganic parts are connected by oxygen bridges. Heating at temperatures of ca. 200 ºC resulted in retaining vibrations of oxygen bridges Si–O–Si only, connected with disappearing of organic parts. Typical results of texture observations are shown in Table 3.

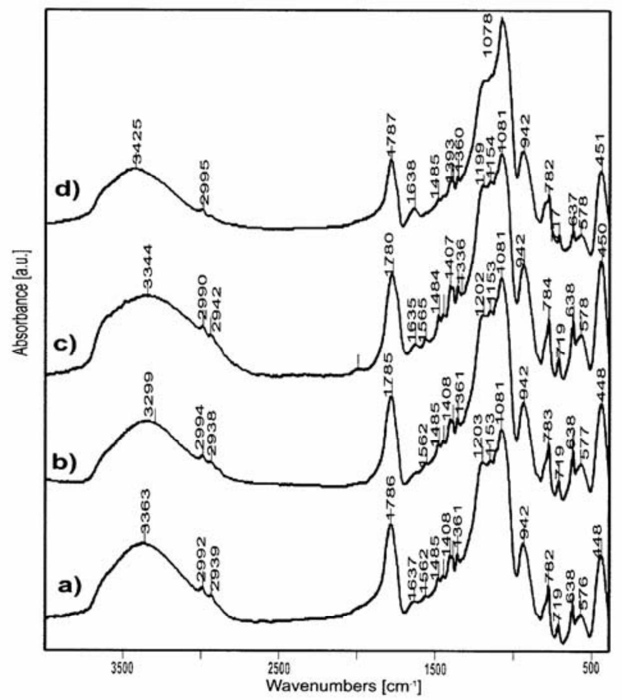

Fig. 2. FTIR spectra of organic-inorganic hybrid gels after heating at 80 ºC:
a) gel C, b) gel B, c) gel K, d) gel D

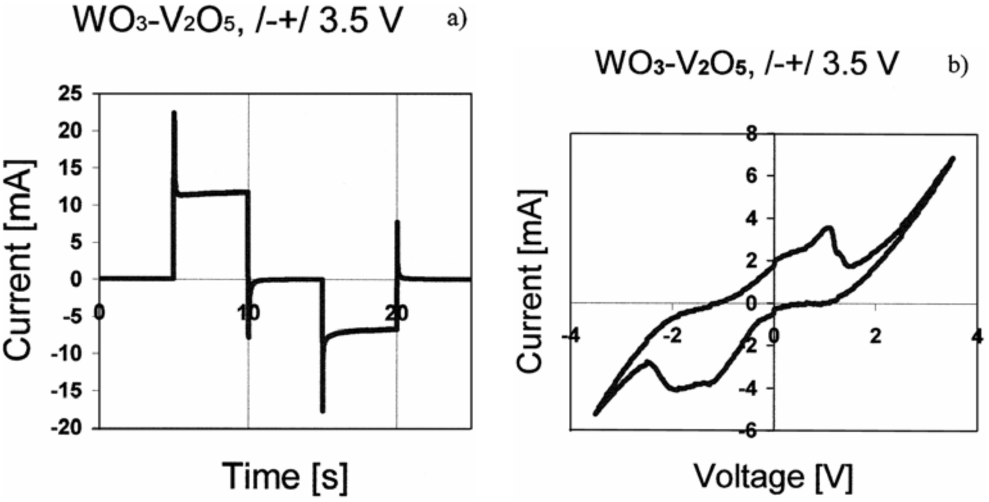

Fig. 3. Current response (a) and cyclic voltammogram (b) for tungsten oxide/hybrid electrolyte, $(LiClO_4)_{0.2}$ $(TEOS/PEO/PC)_{0.8}$/vanadium oxide/thin film electrochromic system on glass coated with fluorine doped SnO_2, after cycling with voltage of ± 3.5 V (cycled area ca. 2 cm^2, scan rate 50 mV/s)

Table 2. Assignments of the characteristic infrared absorption bands [cm^{-1}] [12–15]

B	C	D	K	F	Assignment
448	448	451	450	468	ρ Si-O
576	576	578	576	554	Li in $LiClO_4$ Li with organics
628–638	628–638	637	628	628-638	ClO_4, Li – organics,
719	719	717	720		v SiO–C_2H_5, organics
783	782	782	783	802	v_s Si–O–Si, v_{as} Si–C Si–O–Si–C_nH_m
942	942	942	942	941	v_{as} Si–OH
1081	1081	1078	1081	1090	v_{as} Si–O–Si
1153	1153		1154	1110 1147	v Si–O–Si,
1202	1203		1199		v C–C, –OR (C_2H_5), organics
1361	1361	1360	1392		organics, v CH_3
1393	1393	1393	1407		v CH_2 –O in ethers
1408	1408	1407 1485	1450		
	1562 1637	1638	1565 1635	1639	H–O–H, molecular
1785	1786	1787	1780		organics, C–O
2938	2939	2995	2942		v_{as} CH_2, v C–H_x organic groups
3362	3363 3375	3425	3299	3458	v OH, adsorbed H–O–H,

Table 3. Typical results of texture examination

Material	F	A	B
BET surface area [m^2/g]	248.96	61.84	336.97
Langmuir surface area [m^2/g]	347.87	99.34	484.59
Micro-pore area [cm^3/g]	2.6048	45.82	118.79
BJH meso-pores volume [cm^3/g]	0.4311	–	0.1866
BET micro-pore diameter [nm]	6.7103	1.9357	2.9993
BJH average pore diameter [nm]	5.6562	–	3.7225

dc conductivities at 25 ºC (σ_{25}) for the species A, B, C, D, K and F were of (1.31; 8.29; 1.37; 1.58; 4.26;) $\times 10^{-3}$ $\text{S}\cdot\text{cm}^{-1}$ and 5.6×10^{-5}, respectively. The SEM/EDX, nitrogen adsorption and ionic conductivity examination results have shown that the obtained hybrid materials were porous, with morphologies and conductivities strongly influenced by organic additives and lithium salt doping [16]. In silica glass and silica gel derived materials, both organic additions and doping with lithium, are expected to change coordination of oxygen atoms around silicon and lithium, causing partial dissociation of immobile species from the non-bridging oxygen atoms and also expansion of the silica host, resulting in enlargement of pathways available for lithium ions migration [6–7, 16]. In all of the hybrid gels obtained in this work, both textures and ionic conductivities were generally observed to increase with content of low-molecular-weight organic additives. The enhancement of conductivity was observed especially in samples containing PEO together with addition of PC. These results can be explained in frame of a free-volume model as well as the percolation model, used for fast ion conductive glasses and polymers [4–7].

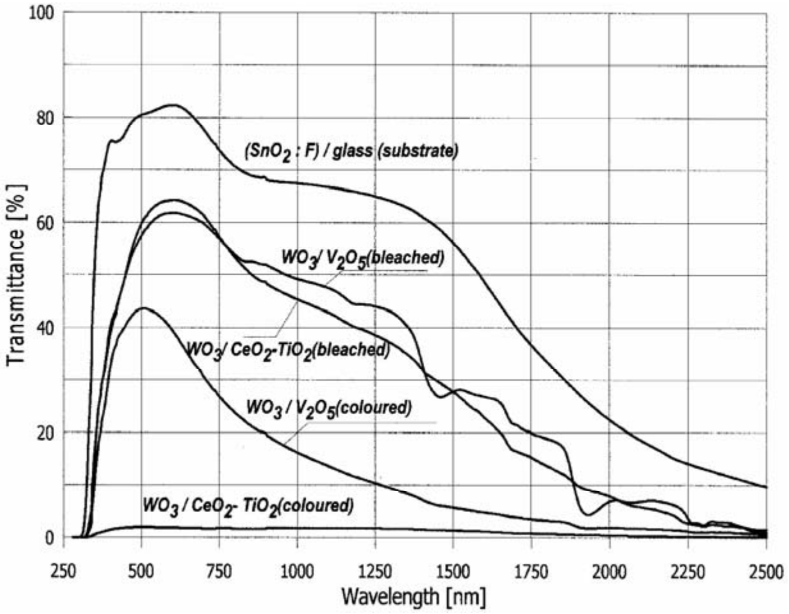

Fig. 4. Transmittance as a function of the wavelength for electrochromic cells with thin films of WO_3 as active electrode and V_2O_5 or CeO_2 –TiO_2 as counter-electrodes, coated by spray pyrolysis onto (SnO_2: F) substrate, and the hybrid organic-inorganic electrolytes examined: C and G, respectively. The spectra were taken for the cells in both lithium intercalated (coloured) and lithium deintercalated (bleached) states, at dc voltage of (±)1.5V and (±)2.5 V, applied to the cells with V_2O_5 or CeO_2–TiO_2 counter electrodes, respectively

Accordingly to relatively large ionic conductivity, of about 10^{-4}–10^{-3} $S\cdot cm^{-1}$, all hybrid gels obtained in this work, when examined in thin film electrochromic WO_3 -based cells have proved to be able to take effective part in reversible electrochromic reactions depending on intercalation/deintercalation of lithium ions associated with injection/extraction of electrons under cycling with low, ± polarized dc voltage and resulting in deeply blue or colourless state of the tungsten oxide layer. A typical current response to a signal of a rectangular shape as well as a cyclic voltammogram (CV) for a cell with electrolyte under investigation are shown in Fig. 3a, b. The symmetric situation and shape of cathodic and anodic peaks for active- and counter-electrode due to ion insertion and extraction respectively, indicate materials under investigation to be kinetically favoured insertion hosts. On the other hand, relatively sharp peaks at the highest values of the voltage applied (in Fig. 3 b, at voltages higher than ca. ± 2.5–3.5 V) makes possible the association of lithium and proton conductance, connected with the presence of water, which has been revealed by infrared spectroscopy in all gels under investigation. Typical photometric transmission characteristics for WO_3-based electrochromic systems with hybrid gels as electrolytes and two different materials of the counter-electrode are given in Fig. 4. The double insertion of lithium ions and electrons into the WO_3 film with active electrochromic properties was accompanied by a significant optical absorption phenomenon which lead to a deep blue colouration due to formation so called tungsten bronze and such electrochromic reactions were reversible.

4. Conclusion

Sol-gel derived, lithium-conducting, organic–inorganic hybrid gel materials obtained in this study from TEOS, PEO, PO and PC precursors, have proved to be electrochemically effective in reversible electrochromic reactions, which make them to be prospective electrolytes for ambient temperature electrochemical and optoelectronic applications. Relatively high room-temperature ionic conductivity, of about 10^{-4}–10^{-3} $S\cdot cm^{-1}$ can be attributed to amorphous character and organic additions. The hybrid structure of the gels obtained in this work, which has been revealed by FTIR investigation, can be ascribed to the formation of bonds between species of organic and inorganic components and incorporation of the organic groups into the silica gel host, resulting in development of structure more accessible for lithium ions migration. With aim to determine exactly a conductance mechanism in electrolytes prepared in this work, further investigations have been undertaken.

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