

Organic-inorganic hybrid electrolytes for thin film metal oxide electrochromic coatings

ELŻBIETA ŻELAZOWSKA^{1*}, MARIA BORCZUCH-LĄCZKA²,
EWA RYSIKIEWICZ-PASEK³, WIESŁAWA LACHMAN¹

¹Institute of Glass and Ceramics, Cracow Branch, ul. Lipowa 3, 30-702 Kraków, Poland

²Faculty of Materials Science and Ceramics, AGH University of Mining and Metallurgy,
al. Mickiewicza 30, 30-059 Kraków, Poland

³Institute of Physics, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27,
50-370 Wrocław, Poland

*Corresponding author: E. Żelazowska; ezelazowska@isic.krakow.pl

Sol-gel derived lithium salt (LiClO₄) doped organic-inorganic hybrid electrolytes have been obtained from the tetraethyl orthosilicate (TEOS) and poly(ethylene oxide) (PEO), propylene oxide (PO), ethyl acetoacetate (EAA), propylene carbonate (PC), polyvinyl alcohol (PVA) precursors and have been investigated for morphology and structural properties by SEM/EDS and FTIR spectroscopy. The hybrid materials obtained were amorphous, with structural properties influenced by organic ingredients which had been used, and with the ionic conductivities of 10⁻⁴–10⁻³ Scm⁻¹. When used as electrolytes in the WO₃ - based thin-film electrochromic coatings, they have proved to be suitable for low-temperature electrochemical applications.

Keywords: organic-inorganic hybrids, sol-gel, lithium-ion conducting electrolytes.

1. Introduction

Solid-state electrolytes with high ionic conductivity of at least 10⁻⁴–10⁻³ Scm⁻¹ order of magnitude at ambient temperatures have recently focused extensive research efforts, because of their potential to be used in rechargeable lithium batteries and for electrochromic displays and smart windows [1–6].

In the last years, the sol-gel process has been widely employed for synthesizing amorphous materials, both inorganic and hybrid organic-inorganic with many interesting properties due to appropriate additives introduced into sols, including organic ingredients for organically modified ceramics (ormocers), silicate materials (ormosils), and electrolytes (ormolytes), both in a monolithic and thin film form [7–12]. Among others, MIYAKE *et al.* [10] have reported on sol-gel derived Nafion/silica

hybrids, and NAKAJIMA *et al.* [11] on the high temperature proton conducting organic/inorganic nanohybrids based on alkoxysilane and polyethylene oxide (PEO), polypropylene oxide (PPO) and polytetramethylene oxide (PTMO) precursors, cross-linked by isocyanato coupling, synthesized for polymer electrolyte membrane fuel cells. Ormolytes of the silica-polyethylene glycol (PEG) system, with ionic conductivities ranged from 10^{-4} – 10^{-2} Scm^{-1} , have been studied by Dahmouche and co-workers [9, 12].

In this work, organic-inorganic hybrid electrolytes have been synthesized from tetraethyl orthosilicate (TEOS), polyethylene oxide (PEO), polyvinyl alcohol (PVA), ethyl acetoacetate (EAA), propylene oxide (PO), propylene carbonate (PC), acetonitrile (CH_3CN), and dichloromethane (CH_2Cl_2) precursors, and have been investigated for morphology and structural properties with the aim to determine the influence of the organic components, especially those with a low molecular weight on structural properties and ionic conductivity of the multicomponent organic-inorganic hybrids.

2. Experimental procedure

Components (at least of reagent grade, Merck and Aldrich) of the starting solutions for gels under investigation are given in Table 1.

Silica components of the gels under investigation were produced by mixing TEOS $\text{Si}(\text{OC}_2\text{H}_5)_4$ and distilled water with the molar ratio of $\text{TEOS}:\text{H}_2\text{O} = 1:4$. As a catalyst,

Table 1. Components of the starting solutions.

Sample	Components	Lithium salt/solvent/fraction	Appearance, remarks
A	TEOS	—	colourless, transparent
B	TEOS, PVA*, EAA	—	colourless, slightly opalescent
C	TEOS, EAA	$\text{LiClO}_4/\text{PC}/0.02$	colourless, transparent
D	TEOS, PVA*, EAA, PO, PC	$\text{LiClO}_4/\text{ethanol}/0.02$	colourless, slightly opalescent
E	TEOS, PVA*, EAA, ethanol	$\text{LiClO}_4/\text{PC}/0.02$	colourless, transparent
F	TEOS, PVA**, EAA	$\text{LiClO}_4/\text{ethanol}/0.02$	colourless, slightly opalescent
G	TEOS, EAA, PEO, CH_3CN , CH_2Cl_2	$\text{LiClO}_4/\text{PC}/0.02$	colourless, transparent
H	TEOS, EAA, PEO, CH_3CN , CH_2Cl_2 , PC	$\text{LiClO}_4/\text{PC}/0.02$	colourless, transparent
J	TEOS, PVA*, EAA, PEO, CH_3CN , CH_2Cl_2 , PC	$\text{LiClO}_4/\text{PC}/0.02$	colourless, slightly opalescent

*PVA with molecular weight $M_w = 72\,000$; **PVA with $M_w = 145\,000$.

36.6% HCl was added drop by drop until pH = 2 was reached. Solutions of the organic parts were prepared separately, using PEO $(-(\text{CH}_2\text{CH}_2\text{O})_n-$, $M_w \approx 600.000$), PVA, EAA, PO ($\text{C}_3\text{H}_6\text{O}$, $M_w = 58.08$), PC ($\text{C}_4\text{H}_6\text{O}$), dichloromethane (CH_2Cl_2), ethanol ($\text{C}_2\text{H}_5\text{OH}$) and acetonitrile (CH_3CN) precursors and solvents. Lithium perchlorate, LiClO_4 in PC or ethanol was used for doping with a weight ratio of about 0.02 with respect to mass of the fresh gel. Mass fractions of the organic ingredients were calculated on ca 30 mass% in gels, at weight concentration of PEO, PVA, PO and/or EAA equal to each other. The pairs of solutions were mixed and stirred for 1 hour before being poured into plastic dishes. Gelation process has occurred within 1–3 days. The samples were dried at ambient temperature for at least two weeks before being heat-treated at temperature of 80°C for 3 hours.

Scanning electron microscopy equipped with energy dispersive X-ray spectroscopy SEM/EDS, (JEOL JSM 5400 with LINK An 10/5) and IR spectroscopy (Bio-Rad FTS-60VM FTIR spectrometer, KBr technique) were used for examination of morphology and structure of the hybrids and pure silica gel obtained in this work. A.c. conductivity was measured with RCL-meter (HIOKI 3532-50 RCL HITESTER).

3. Results and discussion

The names, quality composition and appearance of the hybrid gels obtained and pure silica gel prepared as reference for comparison, are given in Tab. 1. Figure 1 shows typical SEM images (at magnification of $20000\times$) of the hybrid gels under investigation. When examined using SEM/EDS, the morphology of the samples was amorphous and homogeneous.

The spectroscopic FTIR investigation of the hybrid gels under investigation has revealed the presence of absorption bands characteristic of silicon-oxygen bonds,

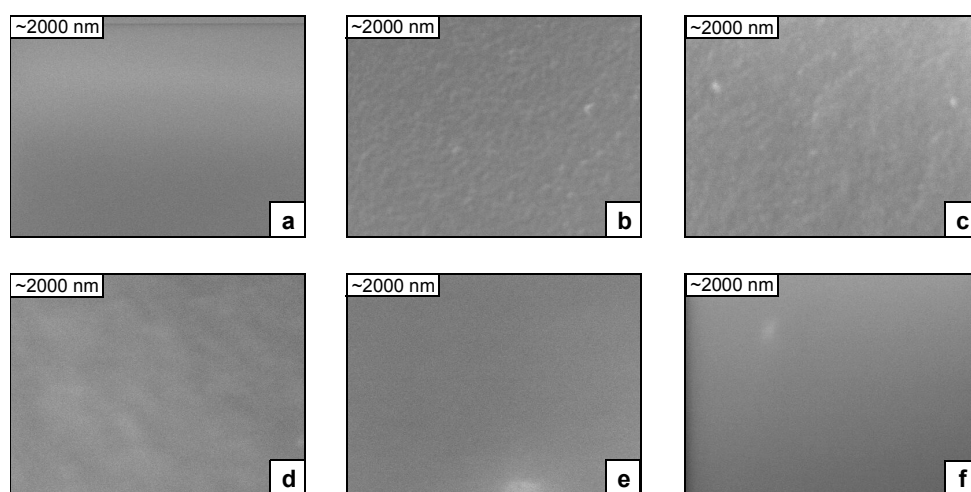


Fig. 1. SEM planar view images of hybrid gels (heated at 80°C): E (a), F (b), G (c), J (d), H (e), A (f).

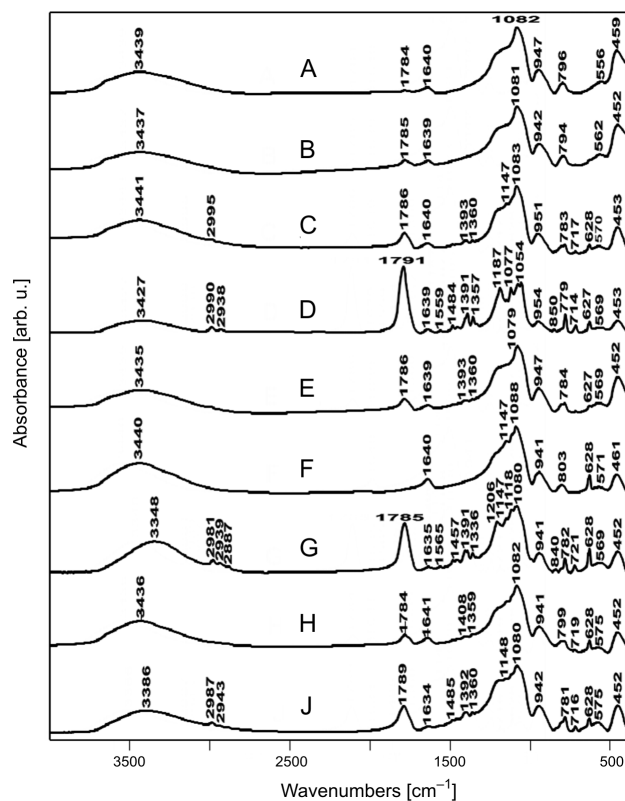


Fig. 2. FTIR spectra of the organic-inorganic electrolytes (B–J) and pure silica gel (A).

organic groups, structural species connected to lithium bonding and molecules of water. Results of the FTIR-analysis (Fig. 2, Tab. 2) are given for samples heated at 80°C, because there were not revealed significant differences between the spectra of hybrid gels taken before and after heating.

Spectra of gels (B) obtained from TEOS with PVA addition were similar to those of pure silica gel and have indicated three fundamental bands characteristic of Si–O vibrations (Si–O asymmetric stretching at about 1000 cm⁻¹, Si–O–Si symmetric stretching at about 800 cm⁻¹ and O–Si–O bending (rock-mode) at about 450 cm⁻¹) [13–16]. The presence of these bands, and especially the band at 800 cm⁻¹, indicates significant degree of polymerization of the SiO₄ tetrahedrons network by means of the oxygen bridges created. The particular vibrations of Si–O* origin (silicon bonded to the non-bridging oxygen) have not been observed there within the framework of the main band at 1000 cm⁻¹. The bands of the organic parts origin were present in the spectrum of the sample before heating and disappeared after heat-treatment. The spectra of gels from TEOS with EAA and LiClO₄ (sample C), are also characteristic of polymerized network of the SiO₄ tetrahedrons but evidently modified due to additives being applied. The sharp band located at 782 cm⁻¹ in the spectra of this gel indicates

Table 2. Assignments of the characteristic bands in FTIR spectra [13–19].

A	B	C	D	E	F	G	H	J	Vibrations origin/structural unit
460	451–452	454	453–454	452	456–462	452	450–452	450	ρ Si–O–Si, bending
560	562	572	572	569	554	570	564	574	Li in LiClO ₄ , Li bonded to organics, Si–O ring (4)
	628	627–637	627	627	628	628–637	627–637	628–638	ClO ₄ ⁻ , Li –organics,
	716	714	714	716	716	716	716	717	Organic parts
	782	779	779	784	784	781–782	784	778–782	O–Si–CH ₃ , Si–O–Si–C _n H _m
795–796	794	795	795	795	796	796	795	790	ν_s Si–O–Si, stretching
958	942	955	956	947	941	942	941–942	947–955	ν_{as} Si–OH, stretching
1079,1082	1081	1080	1054, 1078, 1120, 1187	1079	1088, 1147	1090, 1116, 1147, 1197	1082–1086, 1145	1081, 1199	ν_{as} Si–O, stretching, ClO ₄ ⁻
	1392, 1483	1360, 1406, 1485	1300–1400, 1452	1360, 1393		1359	1359, 1408	1355, 1390, 1456	Organic parts, H in CH ₃ and CH ₂
1641	1639	1643	1640	1693	1641–1643	1643	1643	1558	H–O–H in H ₂ O
1783	1785	1787	1791	1786	1782	1786	1784	1793	Organic parts, C=O
			2939, 2991			2982		2939, 2988	Organic parts, C–H
3456	3445	3444	3437	3435	3500	3422	3442	3421	OH in H ₂ O

the presence of the O–Si–CH₃ groups of the organic-inorganic co-polymers origin, whilst the band at about 628 cm⁻¹ can be assigned to the organic species connected to lithium. The evident splitting of the main absorption band, but observed in the higher wave number range, can be connected with isolation of the vibrations from ClO₄⁻ groups. Besides disappearing of the bands from organic parts, no other differences could be noticed between spectra of gel B before and after heating.

At the presence of the EAA, PO, PC and LiClO₄ (hybrid gel D), practically no peaks corresponding to vibrations from the Si–O–Si bridges have been observed in the spectra of samples, neither before nor after heating. This can be due to an effect of PO and PC additives on an evident decrease in the TEOS poly-condensation reaction. Thus, there in this hybrid gel, the isolated SiO₄ tetrahedrons would be the dominant units in its structure.

The characteristic bands, observed in the spectra of hybrid gels under investigation, correspond to vibrations of ClO₄⁻ groups (1078–1120 cm⁻¹), C–H in the CH, CH₂ and CH₃ groups (2939–2991 cm⁻¹, 1338–1391 cm⁻¹), C=O (1791 cm⁻¹) and OH groups in the H₂O molecules (3421–3500 cm⁻¹), respectively [13–19]. It can be concluded from the absorption spectra of the sample E that increasing of the ethanol and TEOS amounts in the sols instead of PO and PC, results in obtaining spectra with distinct bands at 452, 784 and 1079 cm⁻¹, characteristic of silicon-oxygen network being composed of the SiO₄ tetrahedrons bonded to each other by Si–O–Si bridges. The absorption bands of the organic species and of molecular H₂O origin are also present in the spectra of this hybrid gel. Similar situation, indicating PVA and EAA as organic additives favourable to the reaction of TEOS poly-condensation, takes place in case of sample F. The opposite effect, occurring as a deficiency of distinct bands of the Si–O–Si bridges origin in the spectra of sample G, seems to be connected with the addition of PEO at EAA presence. However the addition of PEO together with PC (sample H) has not negatively affected TEOS poly-condensation ability and creation of the Si–O–Si network. Suppression of the TEOS poly-condensation reaction has also occurred in case of the sample J with more complex matrix, obtained from sols containing PVA, EAA, PEO and PC, although in the spectra of this gel the band at approximately 790 cm⁻¹, commonly assigned to Si–O–Si vibrations and overlapped by the sharp band from O–Si–CH₃ groups, appears after heating [13–16].

A.c. measurements of the ionic conductivities at room temperature for the hybrid electrolytes obtained have revealed values ranging from 10⁻⁴ order of magnitude (samples E and J) to (1.1–7.3)×10⁻³ Scm⁻¹ for samples F,G, D and H (the highest value). Additionally, the hybrid gels obtained in this work were also coated onto glass sheets with thin films of (SnO₂:F) and WO₃, WO₃–TiO₂ and NiO, respectively, and used as electrolytes in the symmetric electrochemical cells of the electrochromic window arrangement at plus/minus polarized d.c. potential of 1.5 V, applied through potentiostat/galvanostat. All the hybrid gels under such examination have proved to be effective in the reversible colouring and bleaching of the WO₃ and WO₃-based electrochromic coatings.

4. Conclusions

Effects of the organic additives and lithium salt doping on morphology and structure of the hybrid organic-inorganic sol-gel derived electrolytes were studied by SEM/EDS and Fourier transform (FTIR) spectroscopy. With the results from the FTIR spectra, it can be stated that:

- the favourable effect on the TEOS poly-condensation possibility was observed for hybrid electrolytes with PVA and EAA additives and also for hybrids with enhanced content of TEOS together with ethanol;
- the influence of the low molecular weight organic additives on structure of the hybrid electrolytes obtained in this work seems to be significantly more complex than plasticizing behaviour observed in the polymer electrolytes based on poly-ethers [20–22].

The most likely this influence can be assigned to the incorporation of the functional groups of the organic species into the TEOS derived network, connected with formation of the strong chemical bonds. Differential affecting of the polymerization reactions in the framework of TEOS-based sols due to organic additives introduced, results in different bonding states and consequently, different structural conditions for ionic charge carrier motions and ionic conductivities [23, 24].

Acknowledgement – Financial support of this work provided by the Ministry of Education and Science, Department of Scientific Research, Poland, Grant No 4 T08D 001 25 is gratefully acknowledged.

References

- [1] BRODD R.J., BULLOCK K.R., LEISING R.A., MIDDAGH R.L., MILLER J.R., TAKEUCHI E., *Batteries, 1977 to 2002*, Journal of the Electrochemical Society **151**(3), 2004, pp. K1–11.
- [2] ZHANG J.-G., BENSON D.K., TRACY C.E., DEB S.K., CZANDERNA A.W., CRANDALL R.S., *Optimization study of solid-state electrochromic devices based on WO₃/lithium-polymer electrolyte/V₂O₅ structures*, Journal of the Electrochemical Society **141**(10), 1994, pp. 2795–800.
- [3] GLÄSER H.J., *Large Area Glass Coating*, Von Ardenne Anlagentechnik GMBH, Dresden 2000.
- [4] FAN J., MARZKE R.F., SANCHEZ E., ANGELL C.A., *Conductivity and nuclear spin relaxation in superionic glasses, polymer electrolytes and the new polymer-in-salt electrolyte*, Journal of Non-Crystalline Solids **172-174**, 1994, pp. 1178–89.
- [5] SHIN J.H., PASSERINI S., *PEO-LiN(SO₂CF₂CF₃)₂ polymer electrolytes*, Journal of the Electrochemical Society **151**(2), 2004, pp. A238–45.
- [6] WANG C., SAKAI T., WATANABE O., HIRAHARA K., NAKANISHI T., *All solid-state lithium-polymer battery using a self-cross-linking polymer electrolyte*, Journal of the Electrochemical Society **150**(9), 2003, pp. A1166–70.
- [7] HAAS K.-H., AMBERG-SCHWAB S., ROSE K., *Functionalized coating materials based on inorganic-organic polymers*, Thin Solid Films **351**(1-2), 1999, pp. 198–203.
- [8] QUARANTA A., CARTURAN S., MAGGIONI G., CECCATO R., DELLA MEA G., *Probing the chemical environment of 3-hydroxyflavone doped ormosils by a spectroscopic study of excited state intramolecular proton transfer*, Journal of Non-Crystalline Solids **322**(1-3), 2003, pp. 1–6.

- [9] DAHMOUCHE K., ATIK M., MELLO N.C., BONAGAMBA T.J., PANEPUCCI H., AEGERTER M.A., JUDEINSTEIN P., *Investigation of new ion-conducting ORMOLYTES: structure and properties*, Journal of Sol-Gel Science and Technology **8**(1-3), 1997, pp. 711–15.
- [10] MIYAKE N., WAINRIGHT J.S., SAVINELL R.F., *Evaluation of a sol-gel derived Nafion/silica hybrid membrane for proton electrolyte membrane fuel cell applications: I. Proton conductivity and water content*, Journal of the Electrochemical Society **148**(8), 2001, pp. A898–904.
- [11] NAKAJIMA H., NOMURA S., SUGIMOTO T., NISHIKAWA S., HONMA I., *High temperature proton conducting organic/inorganic nanohybrids for polymer electrolyte membrane*, Journal of the Electrochemical Society **149**(8), 2002, pp. A953–9.
- [12] DAHMOUCHE K., SANTILLI C.V., DA SILVA M.A., RIBEIRO C.A., PULCINELLI S.H., CRAIEVICH A.F., *Silica-PEG hybrid ormolytes: structure and properties*, Journal of Non-Crystalline Solids **247**, 1999, pp. 108–13.
- [13] GUNZLER H., GREMLICH H.-U., *IR Spectroscopy – An Introduction*, Wiley-VCH Verlag GmbH, Weinheim 2002.
- [14] YING J.Y., BENZIGER J.B., NAVROTSKY A., *Structural evolution of alkoxide silica gels to glass: effect of catalyst pH*, Journal of the American Ceramic Society **76**(10), 1993, pp. 2571–82.
- [15] MUNRO B., *Ion-conducting properties of SiO₂ gels containing lithium salt*, Glass Science and Technology – Glastechnische Berichte **68**(4), 1995, pp. 123–32.
- [16] PRIMEAU N., VAUTEY C., LANGLET M., *The effect of thermal annealing on aerosol-gel deposited SiO₂ films: a FTIR deconvolution study*, Thin Solid Films **310**(1-2), 1997, pp. 47–56.
- [17] PEREIRA A.P.V., VASCONCELOS W.L., ORÉFICE R.L., *Novel multicomponent silicate–poly(vinyl alcohol) hybrids with controlled reactivity*, Journal of Non-Crystalline Solids **273**(1-3), 2000, pp. 180–5.
- [18] JITIANU A., BRITCHI A., DELEANU C., BADESCU V., ZAHARESCU M., *Comparative study of the sol-gel processes starting with different substituted Si-alkoxides*, Journal of Non-Crystalline Solids **319**(3), 2003, pp. 263–79.
- [19] SREEKANTH T., JAIPAL REDDY M., SUBRAMANYAM S., SUBBA RAO U.V., *Ion conducting polymer electrolyte films based on (PEO+KNO₃) system and its application as an electrochemical cell*, Materials Science and Engineering B: Solid State Materials for Advanced Technology **64**(2), 1999, pp. 107–12.
- [20] ŻELAZOWSKA E., ZIEMBA B., LACHMAN W., *Counter electrodes for WO₃-based electrochromic coatings*, Optica Applicata **30**(4), 2000, pp. 663–70.
- [21] WALKER CH.W. JR, SALOMON M., *Improvement of ionic conductivity in plasticized PEO-based solid polymer electrolytes*, Journal of the Electrochemical Society **140**(12), 1993, pp. 3409–12.
- [22] YANG X.Q., LEE H.S., HANSON L.K., MCBREEN J., XU Z.S., SKOTHEIM T.A., OKAMOTO Y., LU F., *X-ray absorption studies of the effect of plasticizers on ion-pair dissociation in a poly(ethylene oxide)-potassium salt complex*, Journal of the Electrochemical Society **142**(1), 1995, pp. 46–51.
- [23] YOFFE A.D., *Electronic properties of low dimensional solids: The physics and chemistry of layer type transition metal dichalcogenides and their intercalate complexes*, Solid State Ionics **39**(1-2), 1990, pp. 1–7.
- [24] DOI A., *Free volumes in several ion-conducting glasses*, Journal of Non-Crystalline Solids **246**(1-2), 1999, pp. 155–8.

Received October 3, 2005