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Application of silicon and titanium alkoxylates as bifunctional additives for composite polymeric electrolytes

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Addition of ceramic grains is widely recognized as an important method for polymer matrix modification. As grain size plays an important role (smaller grains interact stronger), a serious problem appears for nano-sized grains due to their easy agglomeration and difficulties with homogenisation. On the other hand, residual water must be carefully removed from the electrolyte. In this work, we propose a method of simultaneous in-site filler generation and water trapping in the hydrolysis of silicon and titanium alkoxylates. $Ti(OEt)_4$ and $Si(OEt)_4$ used are both commercially available. Conductivity studies were correlated with FT-IR investigations to compare the effect of classical (thermo-vacuum) and chemical drying. Lithium perchlorate and lithium trifluoromethanosulfonate were used as doping salts. Low molecular weight polyglycol in the form of mono- and dimethyl ether was used as the polymer matrix. We observed the influence of drying on ion association in the electrolyte, together with respective conductivity changes. The drying process decreases the conductivity of the composite, whereas filler grain formation increases it. The sign of the final conductivity change varies with the matrix and salt type.

Key words: *composite polymeric electrolyte; ceramic filler; hydrolysis*

1. Introduction

The quest for an ideal polymer matrix for electrolytes is as old as the field itself. No existing materials can fulfil all required properties, including stability, high ionic conductivity, and commercial availability. Thus various methods of matrix modification have been introduced to influence its properties. The main disadvantage of the most popular polymeric host – poly(ethylene oxide) – is its low conductivity resulting from a high content of crystalline phase. It has been widely recognized that the addition of a non-conductive filler such as aluminium oxide or silica leads to ion transport

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enhancement, due to the hindrance of formation of highly ordered regions in the system [1–3]. The influence of grain size, surface area, and the surface groups of the filler were also studied. Later, the influence of the additive on fully amorphous liquid systems containing a polyether matrix was also discovered [4–7]. In this case, the observed change cannot be attributed to phase structure effects, as the pristine system is fully amorphous. Conductivity enhancement in the latter case, however, is limited to a narrow salt concentration range [7]. Changes in the ionic conductivity and microstructure of composite polymer electrolytes result from the Lewis acid-base type interactions between a variety of Lewis acids or base type species present in the system. This comprises acid Lewis centres of the filler, alkali metal cations (being hard acids according to the Pearson classification) [8], anions (being weak Lewis bases), and the base centres of polyether oxygen atoms. Preparation and properties of various types of fumed oxides were discussed in the literature [5] as the starting point for their introduction to liquid composite polymeric electrolytes. Fumed oxides comprising fumed silica, alumina, and titania were synthesized by high-temperature hydrolysis of the corresponding gaseous metal chlorides ($SiCl_4$, $AlCl_3$ and $TiCl_4$) in an O_2/H_2 flame [9, 10]. Due to the pyrogenic synthesis method, all fumed oxides possess unique properties: high-chemical purity [9, 10], nanoscale spherical primary particles (5–50 nm) [11], large specific surface area (up to 600 m^2/g) [11], and nonporous structure [9, 10]. The predominant particle structures are branch-like aggregates (100–500 nm, apparent packing density is about 30% of SiO_2, Al_2O_3, or TiO_2), which cannot be disrupted by shear force and consist of partially fused primary particles (ϕ 10 nm) [11–14].

2. Experimental

The reagents used for the preparation of the reference “dry” samples were carefully dried under vacuum (10^{-5} Torr, 60 hours) prior to use. The drying temperature was 90 ºC for the polyglycols and in the range 110–140 ºC for the salts. The “wet” samples were prepared from commercially available compounds (Aldrich) used without any further purification. The titanium and silicon tetraethoxylates were obtained from Sigma-Aldrich and used as shipped. Despite pristine “wet” sample preparation, all operations were performed in a nitrogen filled dry-box with humidity lower than 5 ppm. ac impedance was recorded with Atlas 98 HI equipment in the 1 Hz–100 kHz range for varying temperatures (20–70 ºC). The obtained data were analysed with Bernard Boukamp’s EQ program to determine the dc conductivity of the samples. FT-IR measurements of the electrolytes were performed on the samples placed between NaCl plates with a Perkin-Elmer 2000 spectrometer with a resolution 0.5 cm^{-1}.

3. Results

A set of FT-IR data is collected in Table 1. For monomethyl capped matrix and lithium triflate salt differences in ion associations can be observed between the wet

(with or without $Si(OEt)_4$) and dry samples. The peak located at 638 cm^{-1}, characteristic of the deformation of the SO_3 salt group, can be divided into parts attributed to free ions and ion pairs forming doublets. For dry samples, it is more asymmetric, showing a higher amount of paired species. Parallel to this, the C–O–C stretching vibration for the wet samples is shifted towards lower wave numbers than for the dry ones (to 1103 cm^{-1} and 1106 cm^{-1}, respectively). The 3 cm^{-1} change can be explained by a weaker coordination of the salt to the polymer chain due to a smaller dissociation rate. A similar and even stronger correlation can be observed for the dimethyl-capped matrix. In this case, for the dry samples, the 638 cm^{-1} peak is divided into a clear doublet, with the second maximum at 641 cm^{-1} confirming stronger ion pairing. A shift for the $\nu_{C–O–C}$ peak is also observed and even more pronounced (Fig. 1). The stronger effect of drying for the dimethyl-capped matrix can be explained by its lower dielectric constant and weaker coordination properties, limited by the absence of free –OH groups. Samples containing $LiClO_4$ exhibit similar changes. One can also observe a splitting of the $\delta_{sc\ CH2}$ peak for the wet samples, almost disappearing for dried samples. Such behaviour confirms a stronger polymer-cation coordination in the more dissociated wet samples.

Table 1. FT-IR data for samples with and without bifunctional additives*

Samplecode	Sample composition	*v* C-O-C [cm^{-1}]	OH peak intensity	Reference intensity	Relative OH intensity
MTJ	PEO–m–$LiCF_3SO_3$	1103	3.25	4.55	1.40
STJ	PEO–m–$LiCF_3SO_3$	1106	2.70	0.19	0.07
MTJ-S	PEO–m–$LiCF_3SO_3$ + TEOS	1103	1.89	1.29	0.68
MTJ-2T	PEO–m–$LiCF_3SO_3$ + 2% TEOT	1106	11.65	0.21	0.02
MTJ-5T	PEO–m–$LiCF_3SO_3$ + 5% TEOT	1106	1.67	0.2	0.12
STJ-S	PEO–m–$LiCF_3SO_3$ + TEOS	1106	–	–	–
MTD	PEO–dm–$LiCF_3SO_3$	1106	2.72	1.90	0.67
STD	PEO–dm–$LiCF_3SO_3$	1108	5.56	0.35	0.06
MTD-S	PEO–dm–$LiCF_3SO_3$ + TEOS	1106	0.62	0.10	0.17
MTD-2T	PEO–dm–$LiCF_3SO_3$ + 2% TEOT	1108	4.35	0.09	0.02
MTD-5T	PEO–dm–$LiCF_3SO_3$ + 5% TEOT	1108	2.61	0.43	0.16
STD-S	PEO–dm–$LiCF_3SO_3$ + TEOS	1108	–	–	–
MNJ	PEO–m–$LiClO_4$	1090	1.14	5.47	4.80
SNJ	PEO–m–$LiClO_4$	1093	4.41	0.58	0.13
MNJ-S	PEO–m–$LiClO_4$ + TEOS	1093	8.95	1.16	0.13
MNJ-2T	PEO–m–$LiClO_4$ + 2%TEOT	1098	9.92	1.56	0.02
MNJ-5T	PEO–m–$LiClO_4$ + 5%TEOT	1095	3.24	0.464	0.14
SNJ-S	PEO–m–$LiClO_4$ + TEOS	1095	–	–	–
MND	PEO–dm–$LiClO_4$	1088	2.57	4.47	1.74
SND	PEO–dm–$LiClO_4$	1090	6.72	0.45	0.07
MND-S	PEO–dm–$LiClO_4$ + TEOS	1090	12.8	0.79	0.06
MND-2T	PEO–dm–$LiClO_4$ + 2% TEOT	1096	10.13	0.41	0.04
MND-5T	PEO–dm–$LiClO_4$ + 5% TEOT	1094	2.11	0.35	0.17
SND-S	PEO–dm–$LiClO_4$ + TEOS	1092	–	–	–

*S – dry reagents, M – wet reagents, TEOS – $Si(OEt)_4$, TEOT – $Ti(OEt)_4$.

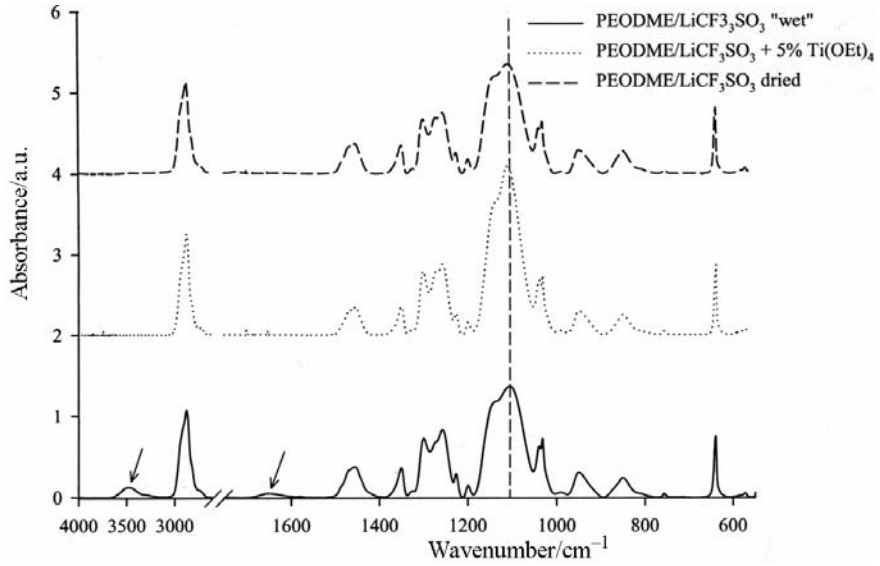

Fig. 1. A comparison of FT-IR spectra for a family of samples with the same polymer matrix and doping salt

In the case of dimethyl-capped polyether, wet samples with the addition of $Si(OEt)_4$ behave identically with the dry ones, thus confirming the efficiency of chemical water removal. The $Ti(OEt)_4$ additive seems to be more effective in water removal when taking into consideration the shift of the peak position. It should be noticed that the position of the ν_{C-O-C} peak is located at lower wave numbers for perchlorate-doped samples than for those containing triflate (respectively 1090–1096 cm^{-1} and 1103–1106 cm^{-1}).

To compare the efficiency of the two drying methods (thermo-vacuum and chemical), a quantitative analysis of the 1650 cm^{-1} peak characteristic of water was performed. The recorded spectra were first baseline corrected. Later, the intensities of the analysed peak were normalized for sample thickness by using a reference peak. For samples containing $LiClO_4$, the band at 1450 cm^{-1} was used as a reference, while the 1350 cm^{-1} peak was used for the ones with $LiCF_3SO_3$. For the $Si(OEt)_4$ additive, the results show that for lithium perchlorate both drying methods are identical in efficiency, leading to about a 30-fold decrease of water content. For lithium triflate, the thermo-vacuum drying leads to water content in the range 5–10% of the start level, while the chemical water removal utilizing $Si(OEt)_4$ is significantly less effective. For a titanium-containing additive, the experiments were performed for samples with two different concentrations of the active compound. Surprisingly, the lower concentration tested is significantly more efficient in the water trapping process. A higher amount of the additive (5 wt./wt. % of the electrolyte) gives worse or comparable results to the thermo-vacuum process, while the lower one produces water contents about five times lower.

Conductivity studies should allow one to easily judge which of the two contrary effects of the process studied is predominant. Introduction of the active compound should decrease conductivity due to water removal. Water traces enhance ionic transport by both decreasing matrix viscosity and by increasing salt dissociation. However, formation of nanosized oxide filler (SiO_2 or TiO_2) grains in the chemical reaction of water with $Si(OEt)_4$ or $Ti(OEt)_4$ is observed, leading to the formation of high conductivity regions. Finally, the overall conductivity of the composite can be either higher, lower, or remain unchanged. In the case of $Si(OEt)_4$ as an additive (see Table 2), the final effect is dependent on the matrix type. For both tested salts and the mono methyl capped matrix, the final conductivity of the composite system is higher than the conductivity of the pristine wet sample. On the contrary, for the dimethyl capped matrix, a decrease of conductivity is observed after adding filler promoter. In any case, the obtained conductivity values were higher in comparison with those of samples obtained by thermo-vacuum drying and not containing any filler. For Ti $(OEt)_4$, a significant increase of conductivity is observed for all studied systems.

Table 2. Conductivity data for samples with and without a bifunctional additives

Sample code	σ [S/cm] at 293 K	E_a [kJ/mol]
MTJ	1.09×10^{-4}	33.5
MTJ –S	1.24×10^{-4}	33.7
MTJ-2T	5.89×10^{-4}	25.6
MTJ-5T	2.64×10^{-4}	25.0
STJ	9.00×10^{-5}	34.0
MTD	1.26×10^{-4}	23.5
MTD-S	9.40×10^{-5}	22.5
MTD-2T	1.76×10^{-4}	22.8
MTD-5T	1.08×10^{-4}	26.0
STD	8.70×10^{-5}	24.0
MNJ	1.11×10^{-4}	39.2
MNJ-S	1.41×10^{-4}	39.4
MNJ-2T	2.73×10^{-4}	30.8
MNJ-5T	2.50×10^{-4}	30.8
SNJ	1.00×10^{-4}	41.0
MND	2.78×10^{-4}	38.1
MND-S	7.65×10^{-5}	40.9
MND-2T	1.55×10^{-4}	25.6
MND-5T	3.35×10^{-4}	26.0
SND	5.32×10^{-5}	44.6

*S – dry reagents, M – wet reagents, TEOS – $Si(OEt)_4$, TEOT – $Ti(OEt)_4$.

The thermal dependence of conductivity exhibits a Vogel-Taman-Fulcher (VTF) shape (see Figure 2). Pseudo activation energies calculated by NLLS fitting to the VTF equation are also collected in Table 2. The values obtained vary in the range

20–40 kJ/mol. The observed differences are significant only for a series of samples with lithium triflate and a dimethyl capped matrix, where the values are around 23 kJ/mol.

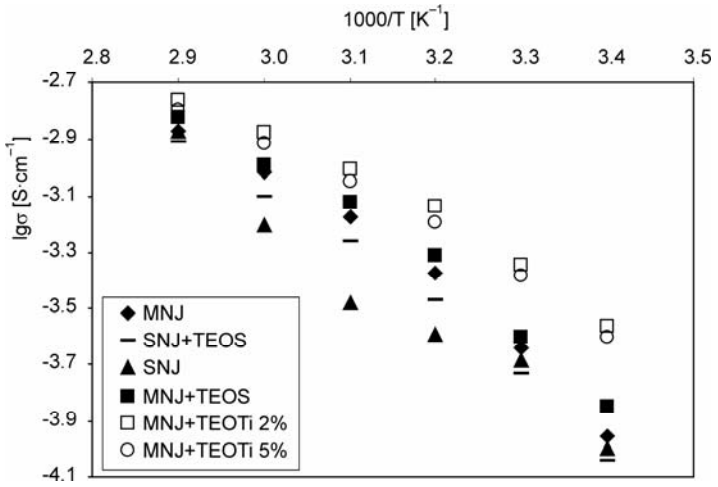

Fig. 2. An exemplary set of thermal dependences of conductivity for a family of samples with the same polymer matrix and doping salt

Within a particular series of samples, neither thermo-vacuum drying nor the addition of $Si(OEt)_4$ cause noticeable changes. The addition of $Ti(OEt)_4$ leads to an observable decrease of activation energy. Only for lithium triflate dissolved in an dimethyl ether matrix do all samples reveal almost identical E_a values.

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