Short communication

Effect of chemically modified silicas on the properties of hybrid gel electrolyte for Li-ion batteries

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Abstract

The aim of the presented work was to perform a preliminary study the physico-chemical properties of hybrid organic–inorganic gel electrolytes for Li-ion batteries based on the PVdF–HFP polymeric matrix and surface modified fumed silicas. Modifications were done by means of the so-called dry method using seven different silanes differing in the nature of the principal functional group: N-2-(aminoethyl)-3-amino propyltrimethoxysilane, 3-glycidoxypropyltrimetoxysilane, 3-mercaptopropyltrimetoxysilane, n-octyltriethoxysilane, 3-(chloropropyl)trimethoxysilane, 3-methacryloxypropyltrimetoxysilane, vinyltrimethoxysilane. The PVdF–HFP gels were prepared according to the so-called Bellcore process (two-step method). Impact of the silicas surface functionality on the degree of crystallinity of the polymeric membranes was studied using the differential scanning calorimetry technique. Applicability of the prepared gel electrolytes for the Li-ion technology was estimated on the basis of specific conductivity measurements. It was shown that modification of the silica surface by most of the silanes causes an increase in the gel specific conductivity by about two orders of magnitude as compared to gel with unmodified silica.
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1. Introduction

Gel-type electrolytes are regarded as a prospective alternative for traditional liquid electrolytes as far as lithium-ion (Li-ion) batteries are considered. Gel electrolytes are obtained by placing some amount of liquid plasticizer and/or solvent in a polymer matrix. This idea was first demonstrated in 1975 by Feuillade and Perche [1] who studied the process of plasticizing a polymer (host matrix) with an aprotic solution containing an alkali metal salt. Since then many different polymers were examined as possible gel matrices, including poly(vinylidene fluoride) (PVdF) [2], poly(acrylonitrile) (PAN) [3,4], poly(methyl methacrylate) (PMMA) [5] and others. The advantage of gel electrolytes over liquid electrolytes lies in the fact that the risk of leakages in the battery systems containing gels is reduced, since in principle no free liquid is present in such systems. In addition to that, their specific conductivities are close to those exhibited by purely liquid electrolytes.

As was demonstrated in the works of Gozdz and Tarascon [6,7] some gel electrolytes can have processing properties that enable successful application in a large-scale production processes. On the basis of their work first reliable, full-scale process (Bellcore process) for manufacturing of liquid-free Li-ion batteries was developed. The novelty of Bellcore process was founded upon application of PVdF/HFP copolymer (where HFP is the abbreviation for hexafluoropropylene) and application of intermediate plasticizer (so-called two-step method of gel preparation). One of the important findings of Gozdz and Tarascon was that addition of highly dispersed silica to the PVdF–HFP matrix significantly enhances the solvent absorption ability, thus leading to a considerable increase in the measured conductivities. The positive effect of various ceramic particles (also Al_2O_3, TiO_2 and others) on the conductivities of dry polymer electrolytes is also well documented in the literature [8–13]. The key factors responsible for the performance of these ceramic additives are believed to be particle size and surface chemistry. Whereas it is widely recognized that, in

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general, nano-scale inorganic particles are more effective than those having micronic dimensions, the influence of the filler surface functional groups remains largely unexplored, especially in case of gel-type electrolytes. Caillon-Caravanier et al. [14] found that addition of unmodified silica provided better mechanical stability and improved the solvent absorption ability of membranes, thus enhancing the conductivities. In more recent works Lee et al. studied the possibility of generating in situ fine silica particles dispersed in the PEO matrix [15] as well as of functionalization of silica surface with glycol chains [16]. Application of crosslinkable silicas modified with certain methacrylate monomers was also reported [17].

In the presented work the influence of surface modified silicas on the properties of gel electrolytes based on PVdF/HFP polymer matrix was studied. Broad range of surface functionalities was examined, including vinylene, glycidoxy, mercapto, chloropropyl, octyl, methacryl and amino groups. The aim of this preliminary approach was to obtain a basic view of how different surface modifications of silica particles affect the degree of crystallinity of the polymer matrix and how is this influence reflected in conductivity measurements. Unlike in the case of most similar works, the applied silicas were not commercial products but were synthesized in the laboratory in analogous conditions, by means of the so-called emulsion method with dry modification [18–20]. This method of silica modification was proved to be successful in introducing the desired functional groups onto the silica surface [21].

2. Experimental

The silicas were prepared in emulsion using the precipitation method with the so-called "dry modification". The syntheses were carried out using two pre-prepared emulsions. The emulsion E1 contained aqueous solution of sodium metasilicate (VITROSILICON S.A.) and cyclohexane (POCh S.A.) while the emulsion E2 contained hydrochloric acid (POCh S.A.) and cyclohexane. In both emulsions non-ionic surfactant was used as an emulsifier. The emulsions were prepared using a homogenizer (19,000 rpm). The process of silica precipitation was conducted using the ULTRA TURRAX T50 Basic homogenizer (IKA-Werke) at 10,000 rpm. In order to change surface character of the produced silicon dioxide, it was subjected to chemical modification using selected alkoxysilanes (10 (w/w) by SiO_2 mass). The applied silane coupling agents are shown in the Table 1. The multimodal particle size distributions were recorded using ZetaPlus apparatus, employing the technique of a dynamic light scattering (DLS). Polydispersity was calculated as a function of particle size distribution. Specific surface areas were determined by N_2 adsorption (BET method) using ASAP 2010 instrument (Micromeritics Instrument Corporation). Samples were heated at 120 °C for 2 h prior to measurements.

The PVdF–HFP gels were prepared according to a method similar to the so-called Bellcore process (two-step method). PVdF/HFP copolymer (Kynarflex, Atofina), was added to acetone together with dibutyl phthalate (DBP) and a given silica. The weight ratio of silica to copolymer was 1:10. The mixtures were stirred vigorously for several hours, followed by 10 min of ultrasonic shaking. The solution was cast on a glass plate, covered by a Petri dish and left for a slow evaporation. The resulting membranes were immersed in diethyl ether and left overnight under stirring to remove DBP, followed by drying at 60 °C under vacuum. Dry membranes were cut into round pieces and immersed in liquid electrolyte solution (1 M $LiPF_6$ in EC/DEC, LP40 Selectipur from Merck). After that, the gel pellets obtained this way were placed in Swagelok-type cells with steel electrodes. The gel pellets were pressed inside the cells with appropriate springs, to provide reliable and reproducible electrical contact in each case. All operations were conducted in dry-box filled with argon.

The XRD measurements were carried out using X-ray diffractometer (Phillips PW-1070) with Cu Kα radiation. The patterns were recorded for $11 < 2\theta < 30$, for the gaps of $1°/1°$, at a counter step of $0.05°$, and for the time of pulse counting of 2 s.

Impact of the silicas surface functionalities on the degree of crystallinity degree of polymeric membranes was studied using differential scanning calorimetry technique (DSC). For the measurements dry membranes (before activation with liquid electrolyte) were taken. The DSC data were obtained between 20 and 280 °C using UNIPAN 610 scanning calorimeter. The samples were heated at 10 °C min^{-1}. Empty aluminum pan was used as the reference.

The conductivities were determined at several temperatures (0–70 °C, the cells were thermostated during measurements) from impedance spectra obtained by means of Solartron impedance analyzer in the frequency range 100 kHz–1 Hz. Typically each measurement was repeated several times to ensure good reproducibility of results.

3. Results and discussion

Modification of silica surface aims at changing its chemical and physical character. The applied silane coupling agents are

Table 1
Symbols, names and chemical formulas of silanizing agents used for modification of silica surfaces

| Symbol	Name	Formula
U-15D	*N*-2-(aminoethyl)-3-amino propyltrimethoxysilane	$H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$
U-222	*n*-Octyltriethoxysilane	$CH_3(CH_2)_7Si(OCH_3)_3$
U-311	3-(chloropropyl)trimethoxysilane	$Cl(CH_2)_3Si(OCH_3)_3$
U-511	3-Methacryloxypropyl-trimetoxysilane	$CH_2C(CH_3)COO(CH_2)_3Si(OCH_3)_3$
U-611	Vinyltrimethoxysilane	$CH_2{=}CHSi(OCH_3)_3$
A-187	3-Glycidoxypropyltrimetoxysilane	$(OCH_2CH)CH_2O(CH_2)_3Si(OCH_3)_3$
A-189	3-Mercaptopropyltrimetoxysilane	$HS(CH_2)_3Si(OCH_3)_3$
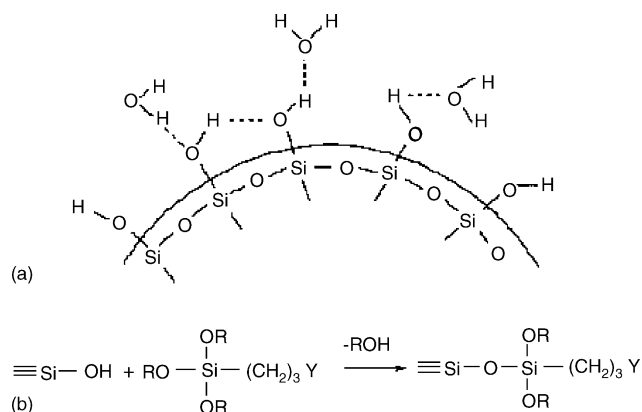
Fig. 1. Schematic representation of a hydrated silica surface (a) and reaction of surface silanol group with an alkoxysilane molecule (b).

Fig. 2. Particle diameter distribution for silica modified with marcapto groups (sample A-189).

proadhesive in character, which means that they are intended to interact with polymer matrix, thus changing the properties of the obtained hybrid organic/inorganic membranes. The silica silanol groups may react with alkoxysilanes according to the scheme shown in Fig. 1. This versatile process enables attaching a broad range of functional groups to the silica surface. The applied modification method differs from the method referred to as "classical" in literature in that the obtained silicas are partially hydrophobized already on the stage of precipitation. In addition to that, the particles have more spherical shape with lower tendency for agglomeration.

Morphological properties of the prepared functionalized silicas are a matter of decisive importance for their performance as components of gel electrolytes. Table 2 summarizes basic characteristics of the materials. Both mean and effective particle diameters of all the examined silicas lie in the range of ca. 400–700 nm (with the exception of sample U-15D, which has much larger particles). Polydispersity, which is the measure of scattering of the individual particle diameters around the mean value, is very low (narrow particle diameter distribution function) for silicas with glycidoksy (A-187), methacryloxy (U-511) and vinyl (U-611) groups (0.005, see Table 2) and attains the highest value for mercapto (A-189) and amino (U-15D) group-modified silica (0.152 and 0.418, respectively). Narrow distribution function seems to be better suited for the application in gel electrolytes. The observed values of mean (and effective) particle diameters may be somewhat misleading in yet another sense. Most of the examined silicas exhibit the feature of the

so-called multimodal (in this case bimodal) particle size distribution, which is clearly visible in the case of sample A-189 (see Fig. 2). A similar pattern is observed for silicas A-187, U-311 and U-511.

It is widely accepted that one of the main factors influencing the ability of a given polymeric membrane to serve as a good host matrix for a gel electrolyte is the degree of crystallinity of this membrane. A powerful method for probing this factor is to measure the specific heat of phase transition (Q_w) related to melting of the crystalline phase by means of differential scanning calorimetry technique. Before the DSC experiments diffraction patterns for all the membranes with modified silicas were obtained (see Fig. 3) in order to verify identity of the crystalline phases in all cases. The peaks at 2θ = ca. 18, 20 and 26.5 can be ascribed to the the crystalline phase of PVdF/HFP copolymer.

The negative values of Q_w are charted on the Fig. 4 for all the dry hybrid membranes (without liquid electrolyte) containing modified silicas. Membrane prepared without any silica addition as well as that containing typical unmodified silica Cabosil were tested as a reference samples. DSC traces for the membranes

Table 2
Morphological characteristics of examined modified silicas

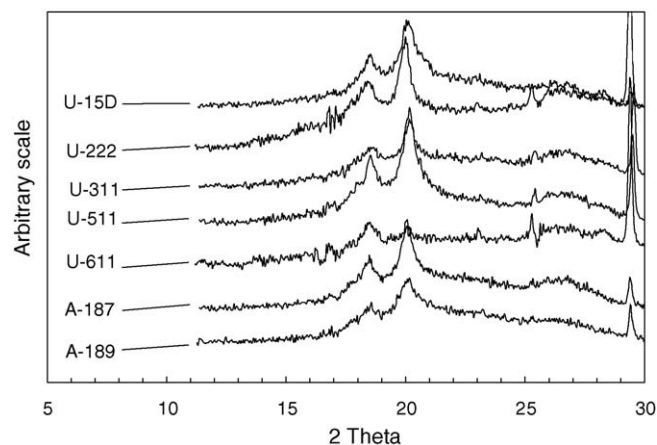| Symbol	Mean particle diameter (nm)	Effective particle diameter (nm)	Polydispersity	BET surface area (m^2 g^{-1})
U-15D	6229	22489	0.418	124
U-222	701	717	0.022	153
U-311	551	473	0.056	140
U-511	540	517	0.005	120
U-611	413	408	0.005	146
A-187	646	502	0.005	117
A-189	711	451	0.152	183

Fig. 3. Diffraction patterns for all the hybrid membranes containing modified silicas.
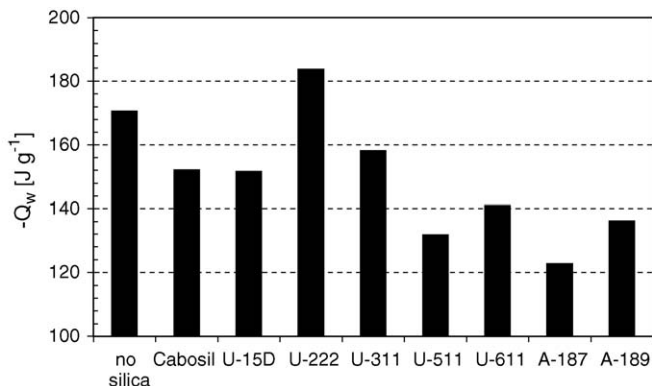
Fig. 4. Specific heats of phase transition for hybrid polymeric membranes with the examined silicas.

Fig. 6. Conductivities measured at 20 °C for gel electrolytes with the examined silicas.

with modified silica can be seen in the Fig. 5. The presented data (Fig. 4) show that addition of any silica (unmodified or modified, with the exception of U-222) results in the decrease in negative Q_w value, which suggests a decrease of crystallinity. The effect is particularly pronounced in the case of silicas modified with glycidoxy (A-187), methacryloxy (U-511) and mercapto (A-189) groups, where reductions of $-Q_w$ by 28%, 23% and 20%, respectively are observed as compared to the silica-free gel. The case of silica with octyl groups (U-222) is very exceptional since a significant increase of crystallinity is observed.

In the Fig. 6 specific conductivities at 20 °C are bar-charted against the type of gel electrolyte. The tendency arising from the presented data is clear. Addition of unmodified silica results in the increase of specific conductivity by about 1.5 orders of magnitude. More than that, practically any functionalization of the silica surface (except for A-187) causes further rise of the conductivity by about 2 orders of magnitude and most conductivities oscillate around $10^{-2}\,\mathrm{S\,cm^{-1}}$. Only in case of silica modified with glycidoxy groups the conductivity enhancement is rather weak. Although the observed beneficial effect of functionalization of the silica surfaces can be partially ascribed to the decrease on polymer matrix crystallinity concluded from DSC measurements, the situation seems to be more complex. Firstly, the A-187 sample which exhibited the lowest crystallinity degree,
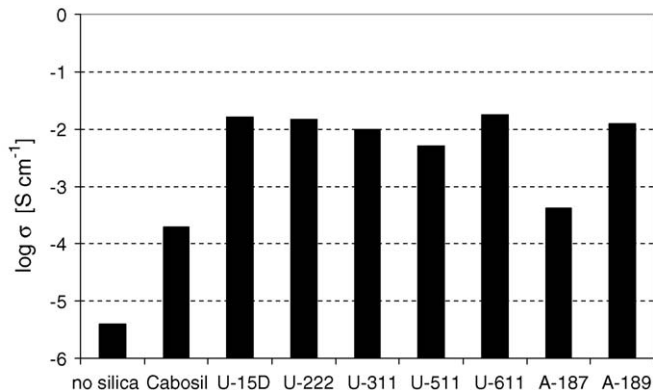
shows the weakest conductivity enhancement (although certain improvement is observed). Secondly, exceptionally high crystallinity of octyl group-modified silica (U-222) apparently has not exerted any detrimental impact on the conductivity. The general conclusion that can be drawn from comparison of Figs. 4 and 6 is that order of crystallinities established on the basis of DSC data is not correlated with the order of conductivities at 20 °C. These observations can give rise to the conclusion that certain other factors beside crystallinity of polymer host matrix influence the gels conductivity performance. It seems to be justified to assume on this early stage of reported investigations that chemical interactions between silica surface groups and the polymer network can have a decisive significance in the overall performance of the described systems. The exact nature of these interactions is yet to be explored in soon-to-be works.

In order to get a deeper insight into the performance of the examined gels the conductivities were measured in a broader range of temperatures. Fig. 7 present temperature dependences of specific conductivities in the form of Arrhenius plots. New knowledge emerges from comparison of Arrhenius plots as far as gels stabilities at higher temperatures are considered. In this respect the studied electrolytes can be divided into two groups. The first one comprises those electrolytes that exhibit drastic
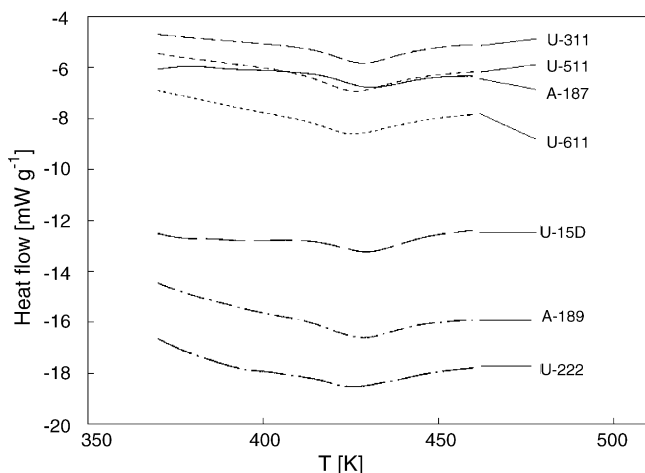

Fig. 5. DSC curves obtained for the dry membranes containing modified silica.
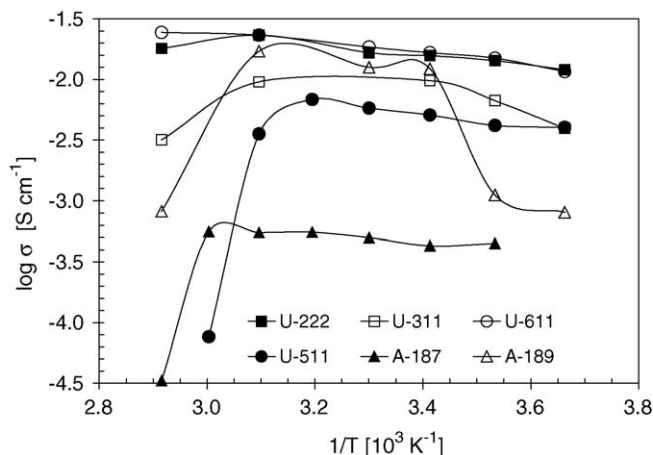

Fig. 7. Arrhenius plots measured for hybrid electrolyte gels containing modified silicas.

decrease of conductivity at the highest temperatures (U-511, A-187, A-189). Within this group an abrupt decline of conductivities by about 1.5–2 orders of magnitude was registered at 70 °C. The rest of gels are characterized by less pronounced decrease of conductivity, or even a fairly stable behavior in the case of silica with vinyl groups (U-611). Instability of gels at higher temperatures should be attributed to the loss of liquid component which leaves the pores of PVdF/HFP matrix. Regarding this, the exceptionally good high temperature stability of U-611 among the studied silicas is particularly interesting since it suggests the occurrence of certain specific interactions between silica functional groups and polymer chain. The observed non-linearity of the Arrhenius plots deserves separate consideration. The phenomenon is likely to be the result not only of liquid electrolyte loss, but also of different conduction mechanisms occurring in the system. Chemical interaction between polymer matrix and silica surface groups may also contribute to the complexity of the observed phenomena.

Further works are in progress, aiming at elucidating the nature of chemical reactions between the silica surface functional groups and polymeric as well as liquid components of the gel electrolytes.

4. Conclusions

The aim of the presented contribution was to present the results of preliminary studies on the application of different surface modified silicas as inorganic fillers for PVdF/HFP-based gel electrolytes. The silicas were synthesized in emulsion with subsequent "dry" modification with a wide range of silanes. Gel electrolytes were prepared on the basis of PVdF/HFP copolymer matrix, using two-step Bellcore method. It was shown that addition of most examined silanized silicas (with the exception of silica with octyl groups) increases the specific conductivities of gel electrolytes by about two orders of magnitude in comparison to unmodified silica and by about 3.5 orders of magnitude compared to the filler-free gel. An important finding is that the positive impact on the specific conductivities has been demonstrated for inorganic fillers characterized by particle diameters of the order of hundreds of microns.

Typically the gel electrolytes with modified silicas prepared within this work were characterized by specific conductivities close to 10^{-2} S cm^{-1} at 20 °C. This general trend is in accordance with the measurements of specific heat of phase transitions

which provided evidence for a decrease of polymer matrix crystallinity in case of most gels with silanized silicas. There is no clear correlation between the degree of crystallinity of the polymer matrix and conductivity of electrolyte based on this matrix within the set of modified silicas. This proves that certain other factors, besides polymer crystallinity, determine the electrolyte conductivity. The presented contribution is by no means complete and leaves a number of questions. More profound investigations are in progress in order to find out what kind of chemical interactions occur in polymer-silica systems. In particular, FTIR technique will be employed for the studies of the nature of chemical bonds between silica surface groups and the polymer matrix. Also, the liquid electrolyte uptake will be determined for the examined dry membranes and the interfacial stabilities of the resulting gel electrolytes will be assessed in the Li|gel|Li cell configuration.

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