

Stability of poly(vinylidene fluoride-*co*-hexafluoropropylene)-based composite gel electrolytes with functionalized silicas

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Abstract

Various aspects of stability of composite polymer gel electrolytes based on poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVdF/HFP) polymeric matrix and functionalized precipitated silicas have been studied. The silica fillers have been surface modified with methacryloxy or vinyl groups by partially replacing silanol groups, so that bi-functional (hydrophilic/hydrophobic) character of the inorganic fillers was created. Compatibility of the gel electrolytes with lithium electrode has been examined by means of EIS technique. Electrochemical stability window has been studied with the application of cyclic voltammetry technique with fast sweeping rate. Passive layer formation on graphite electrode has been investigated for all the gel electrolytes by means of cyclic voltammetry with slow scan rate and galvanostatic charging/discharging technique. It has been shown that stability of the interface between lithium and gel electrolyte is significantly improved when bi-functional silicas are used as fillers. The phenomenon has been ascribed to more effective scavenging of trace impurities as well as to better shielding of the electrode surfaces. Cyclic voltammetry on platinum has revealed excessive electrochemical redox processes upon prolonged cycling for all the gel electrolytes. It has been demonstrated that stable passive layers are formed on graphite electrodes upon electrochemical reduction in the presence of the studied composite polymer gel electrolytes.

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1. Introduction

The electrolytes of potential interest for the technologies of Li-ion batteries may be very roughly classified as liquid (at present most commonly met in commercial products) and polymeric. The later are usually further sub-divided into dry polymer electrolytes, gel polymer electrolytes and composite polymer electrolytes. Since the idea of composite polymer electrolytes (at least those known as so-called mixed-phase composite polymer electrolytes) implies the usage of dispersed ceramic phase (filler) as component of an electrolyte membrane, therefore “gel” electrolytes may simultaneously be “composite”. Both those important categories of electrolytes for Li-ion batteries have been and still are subject of numerous research works. Review articles treating separately the fields of “composite” [1–4] and “gel” [5–6] electrolytes have also been published.

From the structural and functional point of view polymer gel electrolytes can be regarded as intermediate solution between typical liquid electrolytes and so-called “dry” polymer electrolytes. This type of electrolytes compromise advantages and shortcomings of both liquid and polymer electrolytes. They usually exhibit specific conductivities of the order of 10^{-4} to 10^{-3} S cm⁻¹, thus approaching those observed for commercial liquid electrolytes. Apart from that, liquid component of gels is immobilized in a polymer matrix, therefore the membrane as a whole is virtually “solid” in character, and in this way electrolyte leakage from a battery can be to a large extent prevented. From this point of view gel electrolytes may be regarded as viable alternatives for conventional liquid solutions. On the other hand, however, the mentioned liquid components (or plasticizers) present in gels give rise to higher susceptibility towards various redox reactions on the electrodes, which may lead to deterioration of short- and long-term performance of a battery.

Phenomena connected to undesirable oxidation and reduction of species present in the electrolyte systems are all described as their chemical or electrochemical stability. Under this term

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three types of processes are most commonly understood in scientific reports concerning electrolytes for Li-ion cells. The first one is stability towards lithium electrode, usually probed by means of electrochemical impedance spectroscopy (EIS) technique in Li|electrolyte|Li type cells, in terms of time dependencies of the resistance of solid electrolyte interface (SEI) built on lithium electrode in course of chemical reduction of electrolyte species. Another type of “stability” issues relevant to Li-ion battery electrolytes involves their resistance towards electrochemical oxidation. This type of stability is most commonly studied in Li|electrolyte|SS (where SS is stainless steel), or Li|electrolyte|Pt cells using linear sweep voltammetry technique. The onset of an abrupt rise of current density measured on a working electrode indicates the potential at which excessive oxidation of electrolyte species occurs. Although it can be argued that this type of experiment does not perfectly mirror the phenomena observed in real Li-ion cells (different types of positive electrodes are applied in those electrochemical power sources), nevertheless important information may be concluded, especially when comparing characteristics of various electrolytes in the same experimental conditions. Finally, stability of passive layer (solid electrolyte interface) formed on a graphite electrode of a Li-ion cell in the process of cyclic electrochemical reduction of electrolyte components is of significant importance. It is expected that formation of passive layer on graphite should be practically completed in the first charge/discharge cycle and the amount of electrical charge consumed in this process should not be excessively large, so that so-called irreversible capacity of graphite anode associated with it is on a practically acceptable level.

Phenomena related to the stability of composite polymer electrolytes have been studied in the past, however mostly for “dry”, PEO-based systems [1,7–10]. According to the majority of these reports, substantial improvement of stability is always observed after addition of inorganic filler. This effect has been attributed to scavenging trace impurities [9] and shielding the electrode surface, i.e. promoting the formation of smoother and more uniform passive layer [9]. Decreasing of the contact area between electrode and electrolyte has also been proposed as the reason for stability enhancement. On the other hand, Shin et al. [8] have found that no enhancement in the stability of PEO-based electrolyte is observed upon addition of filler when residual solvent and impurities are particularly carefully removed from the membranes. All these studies concern dry electrolyte systems, that is ones that should be free of residual solvents by definition, unlike plasticized systems.

Polymer gel electrolytes based on poly(vinylidene fluoride-co-hexafluoropropylene), designated as PVdF/HFP co-polymer throughout this work, as matrix for liquid phase, have been proved to be among the most promising for practical application in Li-ion batteries. The concept involves the application of microporous co-polymer membranes, in the pores of which conventional liquid electrolyte is immobilized, thus apparently solid electrolyte is obtained. On the basis of this concept reliable technology was elaborated by Bellcore Corp. [11–12]. Later on a number of scientific reports dealing with gel electrolytes with PVdF/HFP polymeric matrix have been published [13–17]. As

was demonstrated in the original, widely cited works of Gozdz and Tarascon [11–12], application of fumed silica as inorganic filler to the co-polymer membranes allows for a very pronounced increase in measured specific conductivities of the resulting electrolyte gels. This phenomenon can to a large extent be attributed to enhanced electrolyte uptake ability of a microporous membrane caused by the existence of highly dispersed ceramic phase, which supports more efficient absorption of the liquid electrolyte. It may be assumed that such factors as size of the silica grains, homogeneity of their distribution in the matrix or surface chemistry of silica particles should influence the performance of an electrolyte gel. Some of these issues have already been addressed, in particular alternative preparation techniques of copolymeric membranes have been reported, leading to somewhat different microscopic structures.

Surface modification of silica by various silane agents has been reported by our group to significantly increase the conductivities of gel electrolytes, however without explaining the actual role of silica surface functionalities [17]. In the present work we further explore the effect of functionalized silica filler addition on the properties of PVdF/HFP composite gel electrolytes in terms of widely understood stability of such electrolytes in electrochemical systems. The objective of this work was to compare the earlier mentioned stability characteristics for the gels containing two kinds of modified silicas (with methacryloxy and vinyl functionalities), as well as for those without any silica filler and with typical unmodified silica.

2. Experimental

2.1. Preparation of composite polymer gel electrolytes

Silica fillers have been manufactured in emulsion. The modification process was made according to so-called dry method. For details of these procedures see the work [17]. Two types of silanes have been applied as modifying agents: 3-methacryloxypropyltrimethoxysilane and vinyltrimethoxysilane. The corresponding functionalized silicas are labeled as SiO₂(met) and SiO₂(vin), respectively. For comparison, typical unmodified silica (Cab-O-Sil, Cabot) have been used in the study, designated as SiO₂(Ø). The three types of silica fillers are listed in Table 1 along with their acronyms used within this work.

Composite polymeric electrolytes have been prepared as in the work [17], according to method similar to the so-called Bellcore process (two-step procedure). PVdF/HFP co-polymer (Kynarfex, Atofina), was added to acetone together with dibutyl

Table 1
Acronyms and specifications of silica fillers used in the work

Acronym	Description	Prevailing type of surface functionality
SiO ₂ (Ø)	Unmodified silica (Cab-O-Sil, Cabot)	None
SiO ₂ (met)	Precipitate silica modified with 3-methacryloxypropyltrimethoxysilane	Methacryloxy
SiO ₂ (vin)	Precipitate silica modified with vinyltrimethoxysilane	Vinyl

phthalate (DBP) and a given silica. The weight ratio of silica to co-polymer was 1:10. The mixtures were stirred vigorously for several hours, followed by 10 min of ultrasonic shaking. After that the mixtures were cast on a glass plate, covered by a petri dish and left for a slow evaporation. The resulting membranes were then immersed in diethyl ether and left overnight under stirring to extract DBP. The membranes were cut into round pieces (ca. 1 cm^2), dried at $60\text{ }^\circ\text{C}$ under vacuum and moved to the dry-box (H_2O less than 20 ppm) where they were subsequently immersed in liquid electrolyte solution (1 M LiPF_6 in EC/DEC, LP40 Selectipur from Merck) to obtain gel electrolytes. The time of soaking was 30 min. After that, the gel pellets obtained this way were placed in Swagelok-type cells with appropriate electrode configuration.

2.2. Experiments in Li|gel|Li cell configuration—electrochemical impedance spectroscopy

Two pellets of metallic lithium (1 cm^2) were sandwiched with a given gel electrolyte separator and placed in a two-electrode cell. Electrochemical impedance spectroscopy measurements were carried out on the cells using Solartron-Schlumberger 1255 apparatus with appropriate current to voltage converter, in the frequency range from 1 MHz to 0.1 Hz with AC amplitude 10 mV. Fitting of impedance responses and determination of resistances were carried out with the application of Boukamp software [18]. Stability of interface between lithium and electrolytes were monitored for 40 days starting from the cell assembly and the measurements were carried out at $25\text{ }^\circ\text{C}$.

2.3. Experiments in Li|gel|Pt cell configuration—cyclic voltammetry

Compared to Section 2.2, platinum discs (1 cm^2) were used instead of lithium as positive (working) electrodes. Cycling voltammetry measurements were carried out using PAR potentiostat/galvanostat, in the potential range of 2–6 V versus lithium counter/reference electrode, at the scan rate of 10 mV s^{-1} . The potential was increased from the cell's rest potential up to the upper potential limit, then the sweep direction was reversed down to the lower limit, followed by reaching back the rest potential. Such cycle was repeated five times (only 1st, 2nd and 5th cycles are presented for clarity).

2.4. Experiments in Li|gel|graphite cell configuration—cyclic voltammetry and galvanostatic charging/discharging

Compared to Section 2.2, graphite electrodes were placed instead of lithium as positive (working) electrodes. SL-20 graphite (Superior Graphite Co.) was used as active material. The graphite active mass was bound with PVdF binder (Fluka, 5% of the overall electrode mixture) and coated onto a copper foil current collectors using a “doctor blade” technique. Cycling voltammetry measurements were carried out using PAR potentiostat/galvanostat, in the potential range of 0–2 V versus lithium counter/reference electrode, at the scan rate of 0.05 mV s^{-1} .

Two potentiodynamic cycles are presented in this work for discussion. Galvanostatic experiments were carried out using Atlas-Sollich multi-channel potentiostat/galvanostat, at the current density of 20 mA per gram of active mass, in the potential range of 0–2 V.

3. Results

3.1. Stability of the phase boundary between electrolyte and lithium electrode

For studying the stability of examined gel electrolytes in contact with lithium electrode experimental conditions described in Section 2.2 have been applied. Fig. 1 shows Nyquist plots recorded for the gels with modified silicas, as well as for the gel without filler and one with typical “unmodified” silica. Spectra recorded after 1st, 17th and 35th day from the cells' assembly reflect the evolution of the phase boundary in time. Depressed semicircles at low/medium frequencies are widely being associated with passive layer and charge transfer resistance, thus constituting the interfacial resistance of the electrode/electrolyte assembly. The shapes of these semicircles in the case of gel without silica and with unmodified silica show signs of substantial instability. In contrary to this, functionalization of the filler particles stabilizes the interfaces. Fig. 2 shows the time dependencies of interfacial resistances (identified with so-called low-frequency resistances R_{LF} determined by fitting the corresponding semi-arcs in the Nyquist plots). The R_{LF} values increase rapidly for the electrolyte without silica and that with unmodified filler, to reach over 80,000 and $15,000\text{ }\Omega\text{ cm}^{-2}$, respectively, after 40 days of annealing in the room temperature. The corresponding values for both modified silica-based gels not only are much smaller (about $400\text{ }\Omega\text{ cm}^{-2}$), but also tend to decrease with storage time.

3.2. Electrochemical stability of electrolytes towards inert electrode

Fig. 3 compares cyclic voltammetry curves (1st, 3rd and 5th cycle are presented) recorded for all the examined gel polymer electrolytes in Li|gel|Pt cell configuration. All characteristics reveal rather complex redox processes, both during anodic and cathodic sweeps. Abrupt increase of current measured on platinum working electrode is observed for all the electrolytes starting from the first cycle at the potentials near 5.5 V versus Li/Li^+ . These signals should be attributed to the irreversible decomposition of liquid electrolyte species. In the first cycle, at potential lower than 5.5 V not very pronounced electrochemical reactions are visible for any of the gels, regardless of the type of filler. In the next cycles, however, distinct current peaks become to evolve on the oxidation sides of the curves, for some of which also cathodic counterparts can be easily identified. Peak at ca. 3.4 V is observed for each of the gel samples and the intensity of this signal apparently increases with the cycle number. Since it is the only reversible current signal detected in the case of gel electrolyte without silica, thus it is assumed to be attributable to polymer matrix itself. Anodic

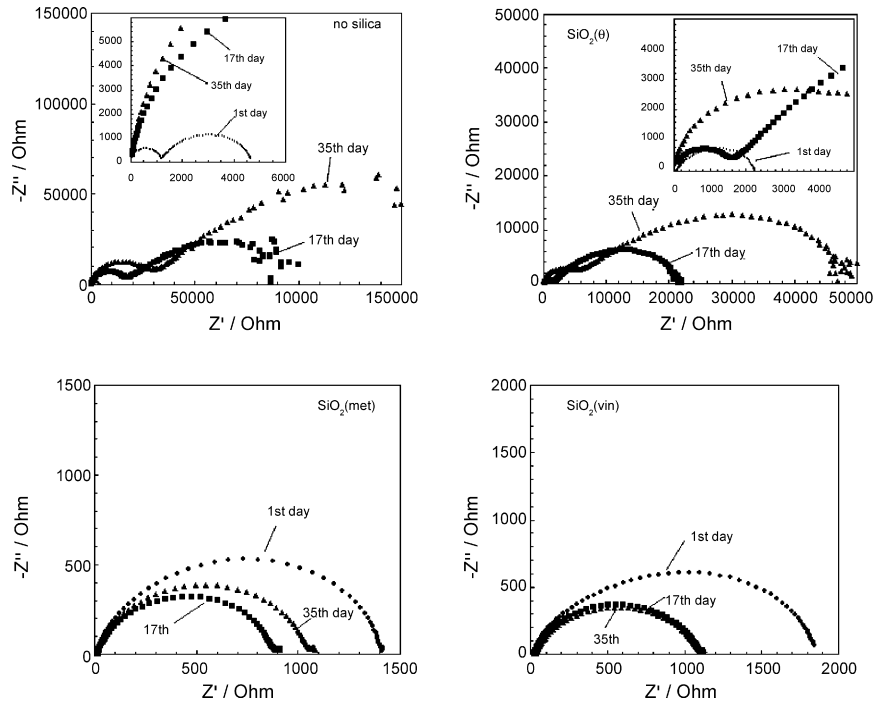


Fig. 1. Nyquist plots recorded for the studied gel electrolytes with silica fillers.

peaks at ca. 3.9 V observed for the gels with unmodified silica and for that with vinyl-functionalized silica should most probably be ascribed to the redox reactions involving fillers. These may be connected either with surface functional group introduced to silica particles (or originally existing on their surfaces) or trace impurities (mainly trace water) trapped by the filler.

3.3. Electrochemical processes on graphite electrode

Phenomena occurring on the graphite electrode (bench-mark anode material for state-of-art Li-ion batteries) have been studied by means of potentiodynamic and galvanostatic techniques. It is expected that conclusions concerning irreversible processes of passive layer formation, as well as reversible intercalation of

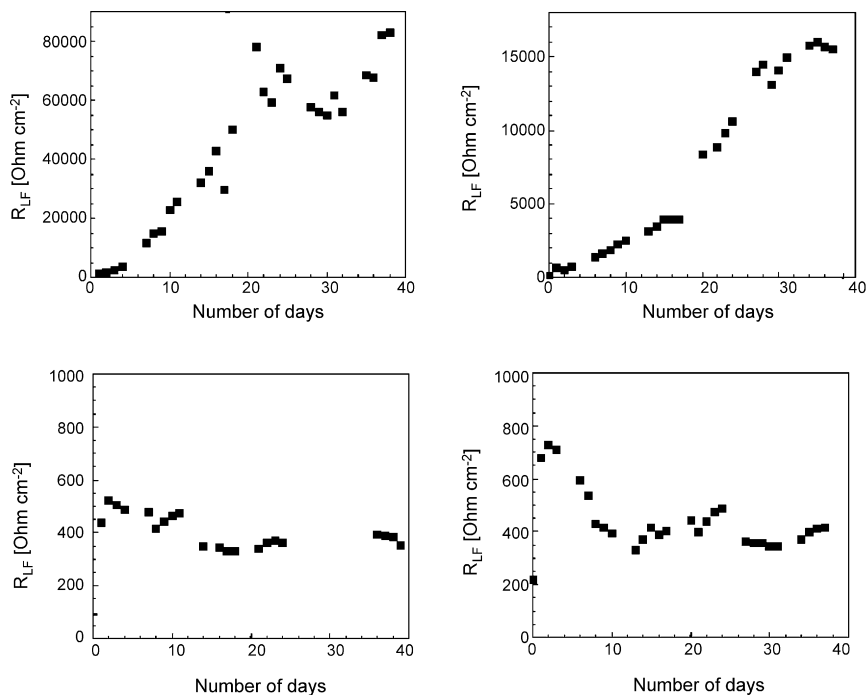


Fig. 2. Time evolutions of the resistances corresponding to the low-frequency semicircles (R_{LF}) determined for the studied gel electrolytes on the basis of their Nyquist plots.

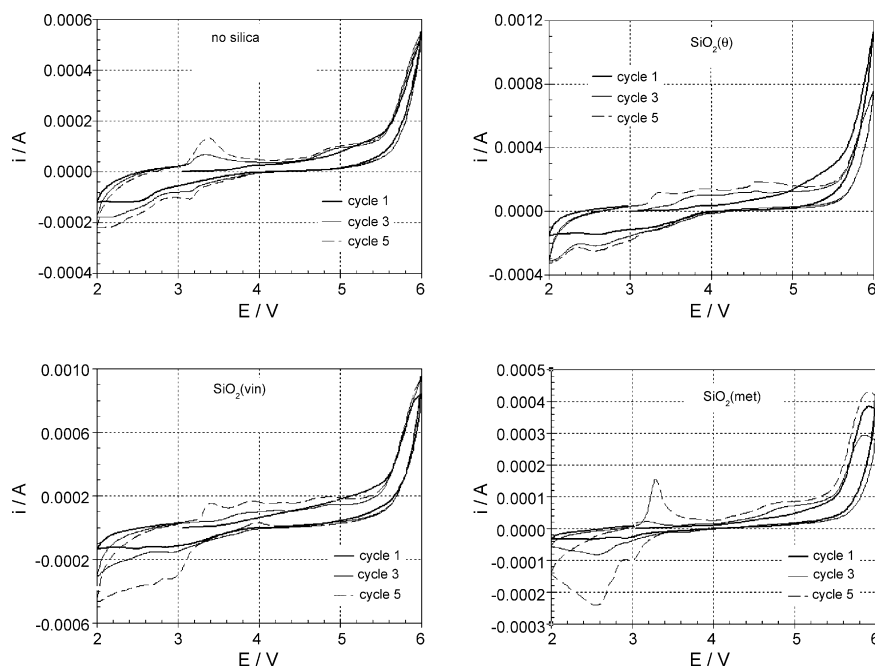


Fig. 3. Cyclic voltammetry curves in Li|gel|Pt cells recorded for the studied gel electrolytes with silica fillers.

lithium ions, will be possible. Fig. 4 shows cyclic voltammetry curves in the first two cycles for all the examined composite polymer gel electrolytes in Li|gel|graphite cell set-ups. The first general remark is that all the systems perform correctly in terms of reversible electrochemical intercalation of Li cations. Current signals corresponding to intercalation and deintercalation of Li^+ are seen (between 0 and ca. 0.4 V) on the cathodic and anodic parts of the cyclic voltammetry loops, respectively, both

in the first and second cycle. Stages of intercalation are reflected as “split” overall deintercalation signals. Going further, current peaks associated with reductive decomposition of electrolyte species on the graphite can be seen as a broad maximum at ca. 0.65 V. The mentioned processes are of great importance for the practical applicability of a carbonaceous anode material for Li-ion batteries, since they are directly correlated with the values of the anode’s irreversible capacities. Additional weaker

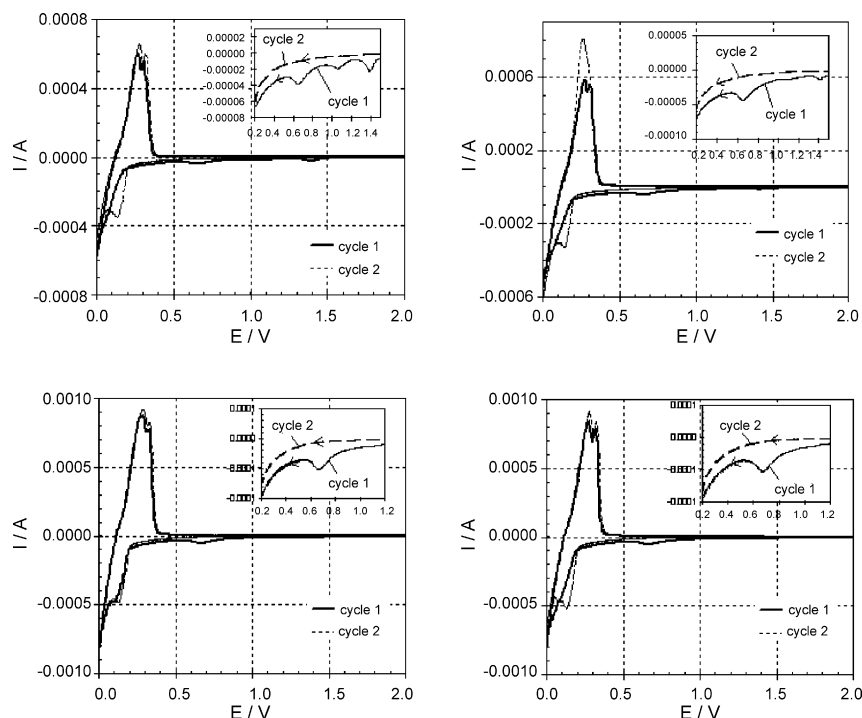


Fig. 4. Cyclic voltammetry curves in Li|gel|graphite cells recorded for the studied gel electrolytes with silica fillers; in the insets—enlarged cathodic parts of the curves for the first two cycles embracing the regions of passive layer formation.

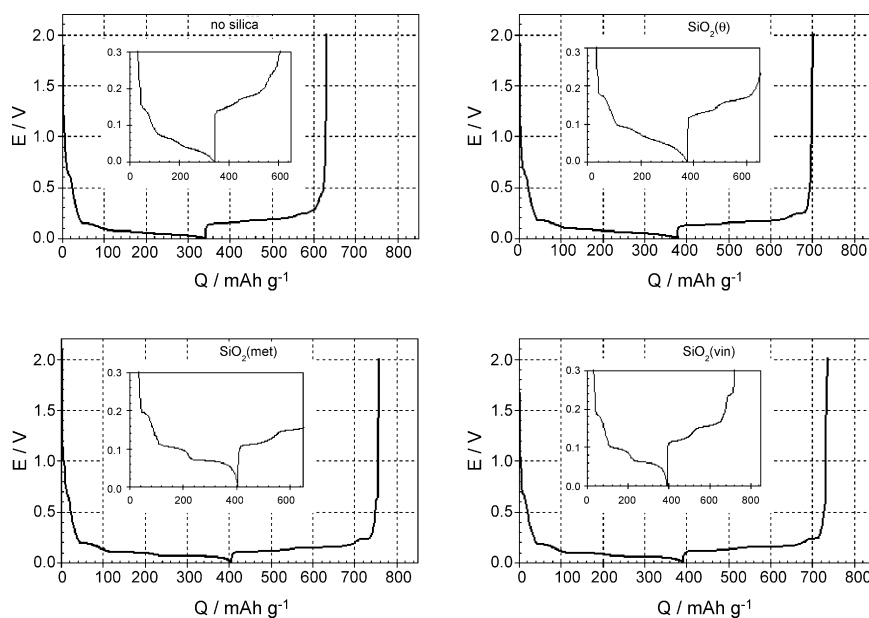


Fig. 5. Galvanostatic charge/discharge curves recorded in Li|gel|graphite cells for the studied gel electrolytes with silica fillers; in the insets—enlarged fragments of the curves displaying the staging phenomena in graphite.

Table 2

Basic electrochemical parameters determined in galvanostatic conditions for graphite electrodes in half-cells with studied gel polymer electrolytes

Type of silica used as filler in a PVdF/HFP membrane	Q_{ch}^1 (mAh g ⁻¹)	Q_{dis}^1 (mAh g ⁻¹)	Q_{irr} (mAh g ⁻¹)	Eff ₁ (%)
No silica	342	299	43	87
SiO ₂ (Ø)	378	325	53	86
SiO ₂ (met)	406	353	53	87
SiO ₂ (vin)	392	345	47	88

Q_{ch}^1 , charge capacity in the first cycle; Q_{dis}^1 , discharge capacity in the first cycle; Q_{irr} , irreversible capacity; Eff₁, efficiency of charging in the first cycle.

reduction peaks (at ca. 1.050 and 1.400 V) are visible on the cathodic parts of first cycle curves in case of gel without filler and that with unmodified silica. These reactions apparently do not occur when functionalized silicas are applied. All the described irreversible electrochemical reactions completely disappear in the second cycles (see insets in the main pictures), which gives rise to the assumption that phase boundaries between graphite electrode and PVdF/HFP gel electrolytes are stable upon cycling, regardless of the filler.

Fig. 5 presents constant current charging/discharging curves in the first cycles for the investigated gel electrolytes, and the basic electrochemical parameters of graphite electrodes tested with these electrolytes are collected in Table 2. The lowest value of reversible capacity in the first cycle (299 mAh g⁻¹) is observed for the case of gel electrolyte without filler. Somewhat higher reversible capacity (325 mAh g⁻¹) has been recorded for the graphite electrode when unmodified silica is present in the gel. Surface modification of the filler results in further increase in reversible capacities (see Table 2), up to the values very close to the maximum theoretical reversible capacities known for graphitic anode materials (i.e., 372 mAh g⁻¹). The trend visible for measured reversible capacities reflects the general trend in specific conductivities reported in the work [17]. In brief: addition of unmodified silica resulted in an increase in conductivity of a gel electrolyte by over 1.5 orders of magnitude,

while using of the majority of functionalized silicas gave rise to further improvement of conductivities by ca. 2 orders of magnitude. Taking into account significantly better developed stages of intercalation in the case of modified silicas (see insets in Fig. 5), one can assume that transport phenomena should be regarded as responsible for the differences in practical capacities measured in Li-ion half-cells. As far as irreversible capacities are concerned, somewhat more of electrical charge seems to be lost on passive layer formation when gel with silicas are used, however the trend is not that consistent. The overall charging efficiency in the first cycle apparently does not depend on the type of filler at all. Between 86 and 88% of the total charge capacity is recovered during subsequent discharge for all the studied polymer gel electrolytes.

4. Discussion

Chemical modification of the silica surfaces applied in this work leads to obtaining the chemical state of silica grains similar to what is depicted in the Fig. 6 for the case of 3-methacryloxypropyl-trimethoxysilane as modifying agent. Important part of surface hydrophilic silanol groups ($\equiv\text{Si}-\text{OH}$) has been replaced by hydrophobic methacryloxypropyl groups (in the case of vinyltrimethoxysilane as modifier vinyl functional groups are present on the silica surfaces). The examined

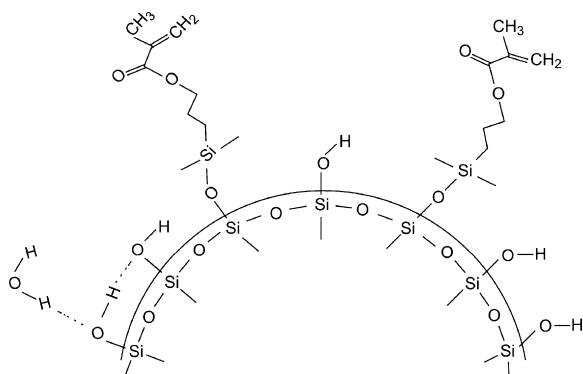


Fig. 6. Schematic representation of the surface of a silica particle modified with methacryloxy functional groups; possible interactions with trace water molecules are depicted.

modified silicas can thus be considered bi-functional as far as their surface chemical state is concerned. Generally speaking, the main prerequisites for the idea of functionalization of silica surfaces may be summarized as follows: (1) partial hydrophobization of the filler surfaces in order to enhance the adhesion between the filler and the polymer matrix, (2) reducing the tendency to agglomeration and (3) narrowing of the filler grain size distribution. Apart from that, in such a specific application as composite polymer electrolytes for Li-ion batteries, one may expect the following positive effects: (4) the ability of trapping trace impurities, such as water, by the remaining silanol groups, thus enhancing long-term stability of the cells, (5) specific interactions with liquid electrolyte species leading to enhanced ion mobility and charge carrier concentrations and (6) suppression of crystallization of the polymer matrix, thus (in case of gel electrolytes) increase in the liquid electrolyte uptake etc. Of course, establishing whether a particular predicted effect really occurs requires appropriate investigation. In the present paper, various aspects of the stability of interfaces are being focused on.

In Section 3.1 it has been demonstrated by means of impedance spectra measured in symmetric Li|gel|Li cells that chemical stability of the lithium/gel interfaces upon prolonged storage is significantly enhanced when modified silica are used as fillers. This effect is in principle independent of the actual type of surface functionality and, interestingly, is not observed in the case of unmodified silica. This suggests that it is surface state of a filler, rather than the existence of a ceramic filler itself, which really matters in terms of enhancement of the compatibility with metallic lithium. Kumar et al. [1] speculated that stability of the phase boundary in the presence of silica and alumina might be related to reactivity of these ceramics with lithium, in terms of negative free energy of corresponding reactions (leading to the formations of Li_2O). In the same work the authors proposed that enhanced stability might arise from scavenging properties of the filler particles toward trace impurities such as water or other liquid solvents. The same explanation has also been put forward earlier by Croce et al. [7]. On the basis of experimental results shown in the present work the theory of scavenging looks much more convincing. Both studied modified silicas contain silanol groups in addition to “nominal” groups (methacryloxy or vinyl), therefore one can expect two

independent effect. The first one is trapping the trace impurities that would otherwise diffuse to the electrode and undergo redox reactions and the second one—suppression of filler agglomeration and thus better screening of the electrode surface (along with larger filler “active” surface). An important conclusion arising from the above considerations is that functionalization of the silica surfaces may give rise to an important enhancement of the system stability in terms of compatibility between lithium and electrolyte.

As far as cycling voltammetry measurements in Li|gel|Pt cells are concerned, a variety of electrochemical reactions detected in the systems, especially in the potential ranges of practical importance for real Li-ion batteries (that is ca. between 2.5 and 4.5 V versus Li/Li^+), should not be ignored. Interestingly, these processes are not that pronounced in the first cycles and become significant not until subsequent cycles. More than that, the observed current signals seem to grow on upon cycling. Most authors reporting results of similar experiments present only one sweep in the anodic direction and on this basis make conclusions concerning anodic stability of electrolytes. From the data presented here for composite polymer gel electrolytes it follows that, perhaps, the issue of electrochemical stability of complex electrolyte systems deserves reconsideration in certain cases.

Considering the behavior of studied gel electrolytes during electrochemical reduction on the graphite electrode (the processes that directly reflect real anode/electrolyte assembly in practical Li-ion cells) one must conclude that the type of filler applied in the composite gel membranes (or lack of thereof) does not affect the process of formation of passive layer on graphite significantly. Additional reduction peaks are observed in case of gel without filler and with unmodified filler (see Fig. 4). It may be assumed that the same entities that improve stability versus lithium for the electrolytes with functionalized silicas, described earlier in this work, also give rise to enhanced resistance towards reduction on graphite. What is more important, SEI formation seems to be entirely completed in the first charge/discharge cycle in all cases, therefore no additional capacity losses are expected upon prolonged cycling of a Li-ion cell. As has already been mentioned in Section 3.3, reversible capacities showed by the graphite electrode in co-operation with examined gel electrolytes are markedly influenced by the electrolyte configuration in terms of filler type and the observed trend simply reflects changes in the gels’ conductivities.

5. Conclusions

Impact of the addition of functionalized silicas on the stability of polymer gel electrolytes based on PVdF/HFP co-polymeric membranes has been studied. The examined silicas are bi-functional in character, which means that part of hydrophilic silanol surface groups have been replaced by hydrophobic methacryloxy or vinyl groups. In terms of compatibility with lithium electrode, both gel electrolytes with functionalized silicas exhibit markedly enhanced stability, not only in comparison with gel electrolyte without any filler but also compared to that with unmodified silica. The observed effect may be related to better homogeneity of filler distribution and lower tendency to

agglomeration, hence improved impurity scavenging and electrode shielding are promoted. As far as electrochemical stability window is concerned, excessive electrolyte species oxidation at potentials above 5 V is observed for all the gel electrolytes on platinum electrodes. Besides, all the electrolytes exhibit a variety of redox reactions in the potential range of interest for Li-ion battery applications. Some of these reactions seem to be reversible. Interestingly, the respective anodic peaks on the cyclic voltammetry traces appear not until the second cycle and grow up quickly upon subsequent cycles. The origin of these current signals remains unclear, they may come from the electrolyte solvents, the salt, trace impurities or surface functionality of filler grains. The manufactured composite polymer gel electrolytes can effectively function in co-operation with graphite anode of a typical Li-ion cell. The measured reversible capacities of graphite (calculated from the galvanostatic cycling) depend clearly on the type of gel and reflect the order of specific conductivities. Passive layer formation on graphite seems to be restricted only to the first cycle in each case, hence the respective interfaces may be described as stable upon cycling.

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