

## Novel composite polymeric electrolytes with surface-modified inorganic fillers

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### Abstract

Surface-modified inorganic powders were applied as additives to plain salt-in-polymer polymeric electrolytes in order to enhance their properties and make them applicable in all-solid-state Li-polymer primary and secondary cells. These fillers consisted of alumina and titania powders (coarse and nano-sized) with superacidic groups introduced onto their surface. Then they were added to low and high molecular weight poly(ethylene oxide) (PEODME 500 and PEO 4,000,000) together with lithium perchlorate (LiClO<sub>4</sub>, lithium tetraoxochlorate(VII)). In this way several different composite electrolytes were obtained that exhibited excellent stability versus lithium metal electrode and high lithium transference number. Herein the preparation procedure is described and preliminary results given.

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**Keywords:** Lithium; Composite polymer electrolyte; Interface; Superacid; Nano-filler

### 1. Introduction

Great flexibility of electric power seems to be the major and crucial advantage of this source, or better—vector of energy. It can be produced in many different ways and can be spent easily in any kind of way—to produce heat, useful work or be used in electronic devices. The sources of electric energy should be light, small and quiet, work at ambient temperature (that can vary strongly), be mechanically strong, provide energy for a long time, at high rates and to have long life. They should be also environmentally friendly and cheap. Until now, the most promising systems are lithium ion cells that employ liquid electrolytes, but these (electrolytes) despite high ionic conductivity have several drawbacks such as safety hazards, instability versus lithium metal (a promising negative electrode) and other low-potential electrodes, need of mechanical separators and strong casing of

the cell, and very limited shape flexibility [1,2]. Thus searches for solid electrolytes that could fulfil all the requirements and be applied commercially. It was found almost 30 years ago [3–5], that polymer based systems could be employed for this purpose and since that moment a lot of effort has been devoted to enhance properties of polymeric electrolytes because they are easy to prepare, cheap and easily applicable in the industrial scale. Until now, most of these studies were directed towards the increase in conductivity of such electrolytes by modifications of polymeric matrices. To this end different polymer architectures were developed by making copolymers, blending different polymers, using inorganic and/or organic fillers [6–17]. It was found that the beneficial influence of inorganic fillers on conductivity of solid CPEs (composite polymeric electrolytes) consists mainly in the lowering of their crystallinity (amorphous phase is a better conductor than the crystalline one).

Various conduction mechanisms for composite polymeric electrolytes were proposed. One of them based on the Lewis acid–base concept was found to be useful to design various types of inorganic fillers bearing Lewis acid groups. It has been demonstrated that the use of such fillers might lead to an enhancement in conductivity even in electrolytes based on amorphous polymeric matrices.

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Recently a new class of fillers with superacid surface groups was developed and its positive effect on the interfacial stability of lithium electrode–polymer electrolyte interface was presented [17]. According to this concept introduction of superacidic groups onto the fillers' surface to immobilise basic species (PEO chains and anions) and promote movement of the acidic ones ( $\text{Li}^+$ ) therefore leading to an increase in cation transference number.

Until now, there is very little information concerning the stability of such systems that is as important as the conductivity, since in a real system, electrolyte remains in contact with low-potential materials (like Li,  $\text{LiC}_6$ , etc.) and can undergo degradation that could cause the cell's failure. The aim of this work was to investigate the influence of novel-type inorganic fillers on the transport properties (particularly lithium transference number) as well as interfacial stability of CPEs.

## 2. Experimental

### 2.1. Fillers preparation and characterisation

Several different fillers were prepared according to the procedure described elsewhere [18,19] (incipient wetness method). In general, three different carriers for sulphate groups were cho-

sen:  $\gamma\text{-Al}_2\text{O}_3$  (Pierce Inorganics BV), P25  $\text{TiO}_2$  (Degussa) and nano-sized  $\text{TiO}_2$  (Kerr-McGee Pigment GmbH). For the sake of convenience they will be called in the text cA, cT and nT, respectively (coarse  $\text{Al}_2\text{O}_3$ , coarse  $\text{TiO}_2$  and nano-sized  $\text{TiO}_2$ ). First two were coarse powders (grain size in the range from 1.02 mm to 1.20 mm), the last one was a fine nano-powder. They were soaked with aqueous solution of sulphuric acid and then dried for 24 h at 333 K and 24 h at 373 K. Acid content (w/w) was 0%, 1%, 4% and 8%. This was followed by 24 h calcination at 773 K in a stream of dry air. Afterwards powders were milled and sieved on a 25  $\mu\text{m}$  opening mesh sieve and dried in a vacuum line—first at RT (for 24 h) and then at 423 K (for 72 h). Pressure was kept below  $5 \times 10^{-7}$  hPa. Then powders were transferred directly (without air exposure) into a dry-box (water concentration below 2 ppm) where they were used for electrolytes synthesis.

These fillers were characterized by XRD (D8 Bruker diffractometer equipped with a Cu anticathode, Ni filter and energy-filtering, superspeed, position-sensitive detector; full pattern matching was made using FullProf software [20]) and SEM (Philips FEI Quanta 200F, with FEG). Species desorbed under heating (in 293–873 K temperature range, with heating rate  $10 \text{ K min}^{-1}$ ) were analyzed by mass spectrometry (QXK 300 quadrupolar mass spectrometer (VG Scientific Ltd.)).

Table 1  
Samples description

Sample no.	Matrix			$\text{LiClO}_4$ conc. (mol/kg of matrix)
	Polymer	Filler	Filler (wt.%)	
1	PEODME 500	–	0.0	0.00
2	PEODME 500	–	0.0	1.00
3	PEODME 500	<25 $\mu\text{m}$ $\text{Al}_2\text{O}_3$ , 0% $\text{H}_2\text{SO}_4$	10.0	1.00
4	PEODME 500	<25 $\mu\text{m}$ $\text{Al}_2\text{O}_3$ , 1% $\text{H}_2\text{SO}_4$	10.0	1.00
5	PEODME 500	<25 $\mu\text{m}$ $\text{Al}_2\text{O}_3$ , 4% $\text{H}_2\text{SO}_4$	10.0	1.00
6	PEODME 500	<25 $\mu\text{m}$ $\text{Al}_2\text{O}_3$ , 8% $\text{H}_2\text{SO}_4$	10.0	1.00
11	PEO 4,000,000	–	0.0	0.00
12	PEO 4,000,000	–	0.0	1.00
13	PEO 4,000,000	<25 $\mu\text{m}$ $\text{Al}_2\text{O}_3$ , 0% $\text{H}_2\text{SO}_4$	10.0	1.00
14	PEO 4,000,000	<25 $\mu\text{m}$ $\text{Al}_2\text{O}_3$ , 1% $\text{H}_2\text{SO}_4$	10.0	1.00
15	PEO 4,000,000	<25 $\mu\text{m}$ $\text{Al}_2\text{O}_3$ , 4% $\text{H}_2\text{SO}_4$	10.0	1.00
16	PEO 4,000,000	<25 $\mu\text{m}$ $\text{Al}_2\text{O}_3$ , 8% $\text{H}_2\text{SO}_4$	10.0	1.00
21	PEODME 500	<25 $\mu\text{m}$ $\text{TiO}_2$ , 0% $\text{H}_2\text{SO}_4$	10.0	1.00
22	PEODME 500	<25 $\mu\text{m}$ $\text{TiO}_2$ , 1% $\text{H}_2\text{SO}_4$	10.0	1.00
23	PEODME 500	<25 $\mu\text{m}$ $\text{TiO}_2$ , 4% $\text{H}_2\text{SO}_4$	10.0	1.00
24	PEODME 500	<25 $\mu\text{m}$ $\text{TiO}_2$ , 8% $\text{H}_2\text{SO}_4$	10.0	1.00
25	PEODME 500	Nano- $\text{TiO}_2$ , 0% $\text{H}_2\text{SO}_4$	10.0	1.00
26	PEODME 500	Nano- $\text{TiO}_2$ , 1% $\text{H}_2\text{SO}_4$	10.0	1.00
27	PEODME 500	Nano- $\text{TiO}_2$ , 4% $\text{H}_2\text{SO}_4$	10.0	1.00
28	PEODME 500	Nano- $\text{TiO}_2$ , 8% $\text{H}_2\text{SO}_4$	10.0	1.00
29	PEO 4,000,000	<25 $\mu\text{m}$ $\text{TiO}_2$ , 0% $\text{H}_2\text{SO}_4$	10.0	1.00
30	PEO 4,000,000	<25 $\mu\text{m}$ $\text{TiO}_2$ , 1% $\text{H}_2\text{SO}_4$	10.0	1.00
31	PEO 4,000,000	<25 $\mu\text{m}$ $\text{TiO}_2$ , 4% $\text{H}_2\text{SO}_4$	10.0	1.00
32	PEO 4,000,000	<25 $\mu\text{m}$ $\text{TiO}_2$ , 8% $\text{H}_2\text{SO}_4$	10.0	1.00
33	PEO 4,000,000	Nano- $\text{TiO}_2$ , 0% $\text{H}_2\text{SO}_4$	10.0	1.00
34	PEO 4,000,000	Nano- $\text{TiO}_2$ , 1% $\text{H}_2\text{SO}_4$	10.0	1.00
35	PEO 4,000,000	Nano- $\text{TiO}_2$ , 4% $\text{H}_2\text{SO}_4$	10.0	1.00
36	PEO 4,000,000	Nano- $\text{TiO}_2$ , 8% $\text{H}_2\text{SO}_4$	10.0	1.00

## 2.2. Electrolytes preparation and characterisation

Poly(ethylene oxide) dimethyl ether, average molecular weight 500 g/mol (PEODME 500, Sigma–Aldrich) that is liquid at RT was filtered and dried in a vacuum line at 333 K for 72 h. It was also freeze-dried using freeze-pump-thaw cycles. Liquid nitrogen bath was the coolant. Dry PEODME 500 was transferred under vacuum to the dry-box where it was used. Poly(ethylene oxide) average molecular weight  $4 \times 10^6$  g/mol (Sigma–Aldrich) was dried in a vacuum line, first at RT for 24 h and then at 343 K for 72 h. Dry PEO 4,000,000 was transferred under vacuum to the dry-box where it was used. LiClO<sub>4</sub> (lithium perchlorate, lithium tetraoxochlorate(VII)) (Sigma–Aldrich, reagent grade) was ground in a mortar and dried in a vacuum line, first at RT for 24 h and then at 373 K for 72 h. Dry LiClO<sub>4</sub> was transferred under vacuum to the dry-box where it was used. In all cases pressure was kept below  $5 \times 10^{-7}$  hPa. A new bottle of acetonitrile (Sigma–Aldrich, HPLC grade), was opened only inside the dry-box and used as received.

Twenty-eight different samples were prepared according to Table 1. In case of liquid electrolytes (thereafter L), polymer, salt and fillers were closed in hermetic jars and stirred inside the dry-box on a magnetic stirrer at 323 K for 2 weeks before taking any measurements. Solid electrolytes (thereafter S) were prepared by casting method. The polymer was dissolved in acetonitrile and then the salt and filler were added. Solutions prepared in such a way were closed in hermetic jars and stirred on a magnetic stirrer at 323 K in the dry-box for 1 week. In the mid-time, solutions were placed in an ultrasonic bath outside the dry-box to pulverize visible fillers' aggregates. Then warm, faintly milky solutions (of low viscosity) were casted on Teflon<sup>®</sup> crystallisers inside the dry-box, for acetonitrile evaporation. These were placed in a levelled box, containing X13 molecular sieves to prevent the dry-box atmosphere contamination with excess of CH<sub>3</sub>CN [21]. After several days of drying, the obtained self-standing foils were dried under vacuum for 24 h at 333 K. They were mechanically strong and uniform in thickness ranging from 40 μm to 60 μm. Weights of all foils prepared were checked in order to ensure if CH<sub>3</sub>CN has totally evaporated. This was confirmed within the balance precision. Such electrolytes correspond roughly to Li(EO)<sub>20</sub> composition (except #1 and #11).

Conductivity measurements were made using complex impedance method [22] in a wide temperature range. Samples were put between stainless steel blocking electrodes and their impedance was followed using computer-interfaced Solartron-Schlumberger 1255 frequency response analyzer, in 100 kHz–1.00 Hz frequency range with 9 mV signal amplitude. Temperature was controlled using HAAKE K75 cryostat-thermostat with HAAKE DC50 temperature controller. Samples were conditioned for 1 h at each temperature before recording impedance spectra.

Lithium cation transference number was obtained by the dc polarisation method [23,24] using a PARSTAT (Princeton Applied Research) potentiostat–galvanostat with frequency response analyser. Potential step of 50 mV across the cell,

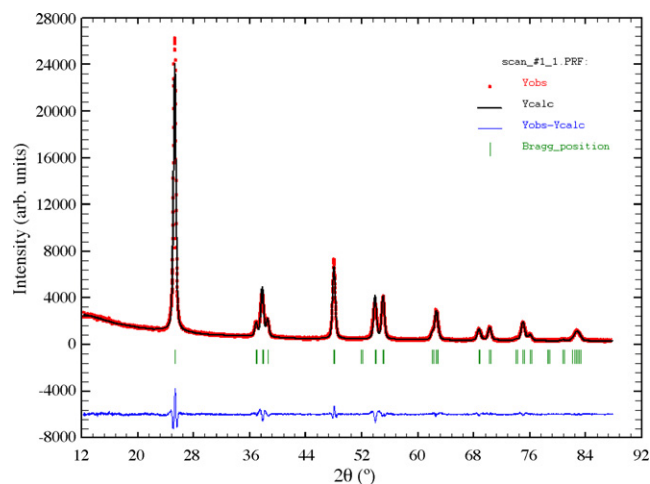


Fig. 1. Fitting of the XRD pattern of nano-TiO<sub>2</sub> + 8% H<sub>2</sub>SO<sub>4</sub>, after the heat treatment; reflections indicated correspond to *I4<sub>1</sub>amd* space group (anatase).

with 4 ks duration was applied, current was recorded every 4 s. Just before and after the step, EIS spectra were recorded in 100 kHz–100 mHz frequency range with 9 mV signal amplitude. Temperature was  $310 \pm 1$  K. These measurements were repeated four times in 24 h intervals, using the same sample. Symmetric Li–Li cells with several of the electrolytes studied were prepared in so-called Swagelok cells. Li metal discs (12 mm in diameter, 400 μm thick, Sigma–Aldrich) were sandwiched on both sides of the electrolyte and this stack was placed between stainless steel current collectors. In case of liquid samples a polypropylene ring was used as a spacer that was filled with the liquid electrolyte.

The electrochemical characterisation of lithium–electrolyte interface was studied using VMP2 Multichannel Potentiostat (Biologic Science Instruments) by recording impedance spectra in 200 kHz–10 mHz frequency range with 9 mV signal amplitude. Symmetric Li–Li cells with several of the electrolytes studied were prepared in so-called Swagelok cells as described above. Since temperature has a great influence on the impedances of these electrolytes (particularly of solid ones), their evolution was examined in temperature-controlled environment. Cells with liquid electrolytes were kept at 293 K in an air-conditioned room, whereas those with solid ones were put in an oven set at 328 K (this increased temperature made measured impedances lower and thus easier to measure, moreover aging phenomena were accelerated making these data more reliable<sup>1</sup> than if they were obtained at RT). Evolution of the impedance was examined by recording impedance spectra every several hours.

Further characterisation of lithium–electrolyte interface was studied using Philips Scanning Electron Microscope with X-ray microanalysis detector (EDS) and unique sample transfer system [25] allowing sample transfer from a dry-box to the microscope without any air exposure.

<sup>1</sup> Assuming that Van't Hoff rule could be applied to describe the kinetics of phenomena taking place at the Li–polymer interface, 10–100 times longer time would be needed to obtain similar results by making these experiments at RT.

Electrochemical stability of the electrolytes was examined by recording cycling voltammograms [22] in a three-electrode Swagelok-type cell. The working electrode was Pt disc, the counter electrode was Au disc and the reference electrode was a Ta wire. Data were collected for  $-3\text{ V}$  to  $+3\text{ V}$  versus Ta potential range at  $10\text{ mV s}^{-1}$  scan rate. Cells were kept in the cryostat at  $328.15\text{ K}$  and connected to PARSTAT (Princeton Applied Research) potentiostat–galvanostat.

### 3. Results and discussion

#### 3.1. Fillers

X-ray diffraction showed no new phases after treatment with acid (Fig. 1). Anisotropic refinement of XRD patterns for nano-fillers brought crystallites' average size before and after

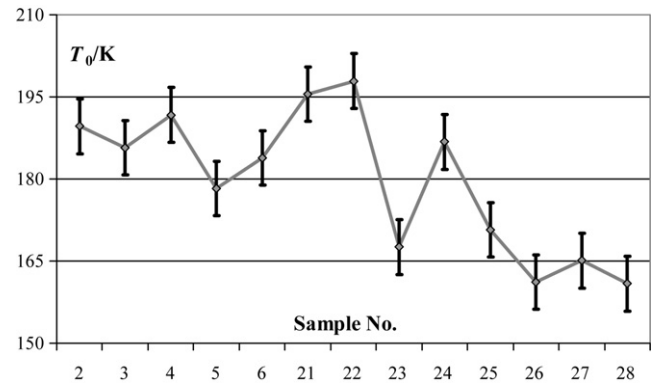


Fig. 3.  $T_0$  values from VTF fitting.

preparation procedure being around  $10\text{ nm} \times 10\text{ nm} \times 50\text{ nm}$  and  $50\text{ nm} \times 50\text{ nm} \times 100\text{ nm}$ , respectively. TEM micrograph confirmed the initial grain size, SEM pictures of the calcined powders showed important agglomeration, but even these agglomerates' sizes were in submicron range. In case of coarse fillers no new phases appeared, either. SEM showed that average grain size was  $10\text{ }\mu\text{m}$  or so. Mass Spectra recorded at up to  $873\text{ K}$  showed only peaks at  $m/z = 14, 28, 16, 32$  coming from air (nitrogen and oxygen) flown into the system (and minor ones at 40 and 44 corresponding to argon and carbon dioxide) and at  $m/z = 1, 17, 18$  coming from water desorption. It is to point out that there were no peaks that could originate from surface sulphate groups [18] and all the acid added remain on the filler surface although heat treatment temperature is well above sulphuric acid boiling point, as it was proven by XPS in the same study where the superacidic character of these powders was studied [18].

#### 3.2. Conductivity

Impedance spectra consisted of a HF semicircle with LF spike. They were fitted with Equivalent Circuit by Boukamp<sup>TM</sup> [26,27]. For PEODME 500 based samples (L) with coarse fillers, shoulders were systematically observed at the LF spikes that were attributed to fillers' particles sedimentation within the cell. They were not observed in other cases.

As one can see (Fig. 2), for L samples, conductivity in liquid state is not affected by the presence of fillers. Differences

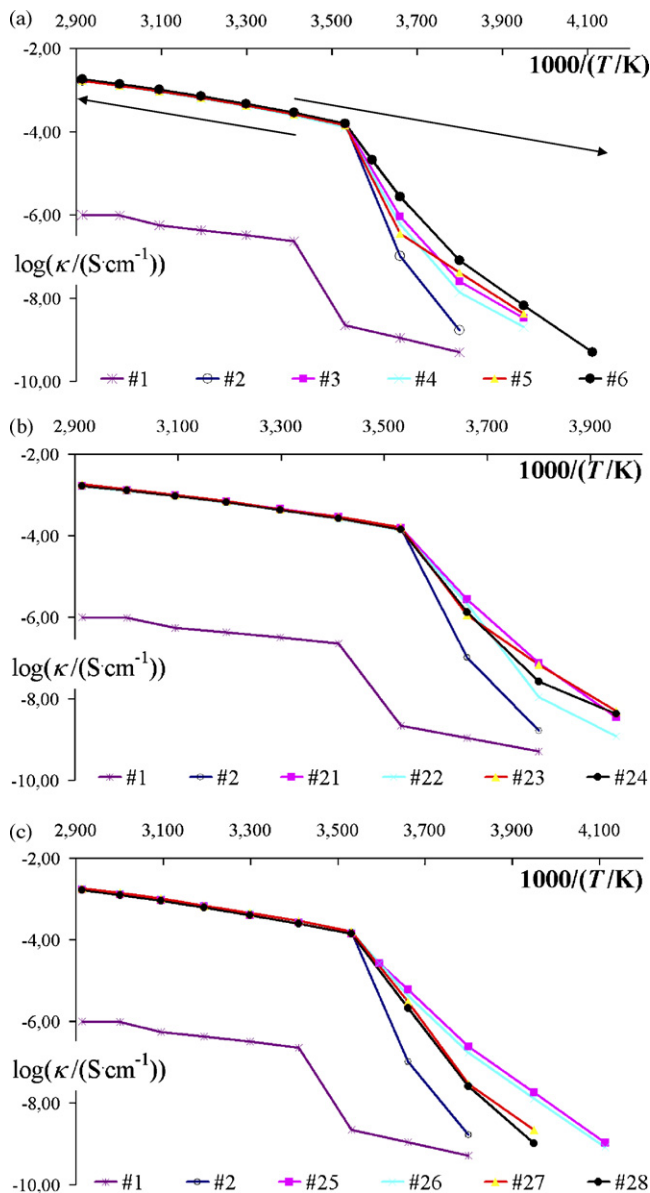


Fig. 2. Conductivities of PEODME 500-based samples: (a) with cA, (b) with cT, (c) with nT.

Table 2  
Transport numbers from dc experiments

Sample	$T_+$			
	Day 0	Day 1	Day 2	Day 3
2	<b>0.31</b>	0.96	0.94	0.94
21	<b>0.80</b>	0.90	0.82	0.85
22	<b>0.88</b>	0.80	0.83	0.85
23	<b>0.90</b>	0.80	0.90	0.83
24	<b>0.77</b>	0.76	0.68	0.80
12	<b>0.32</b>	0.52	0.77	0.76
29	<b>0.61</b>	0.73	0.80	0.79
30	<b>0.66</b>	0.76	0.79	0.73
31	<b>0.72</b>	0.78	0.77	0.79
32	<b>0.77</b>	0.79	0.74	0.77

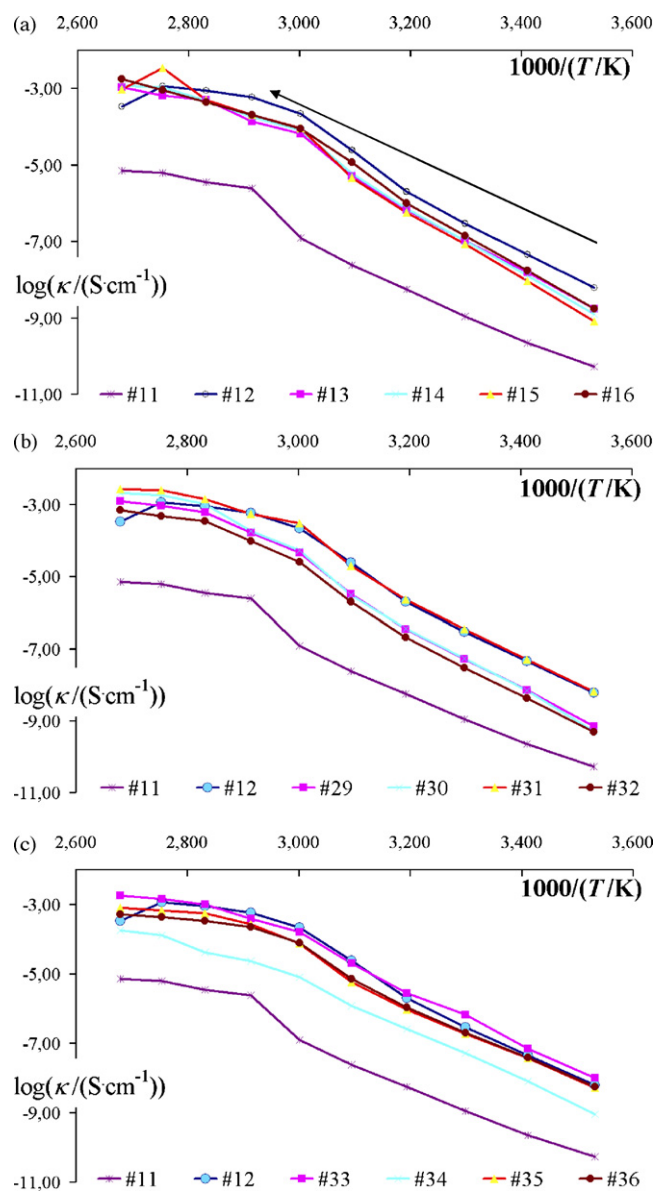


Fig. 4. Conductivities of PEO 4,000,000-based samples: (a) with cA, (b) with cT, (c) with nT.

are in the range of uncertainty limits. But when we move to temperatures below polymer melting point, large differences appear between reference sample (#2) and composite ones. It is because the presence of fillers strongly influence the crystallisation process and electrolyte is believed to be amorphous (or multi nano-crystalline [28], since there are very many nucleation centres and resulting crystallites are very small with large fraction of grain boundaries) instead of crystalline. Also the cooling rate seems to have major influence on the conductivity values (for samples #6, #25 and #26 it was much lower<sup>2</sup> in the phase transition range:  $0.5 \text{ K min}^{-1}$  between 283.15 K and 273.15 K). Thus link between conductivity and structure is confirmed once again.

<sup>2</sup> Although equilibration times were quite long (1 h), cooling and heating rate of the cryostat was usually in the range of  $10 \text{ K min}^{-1}$ . For lower cooling rate, labour and time-consuming manual control was required.

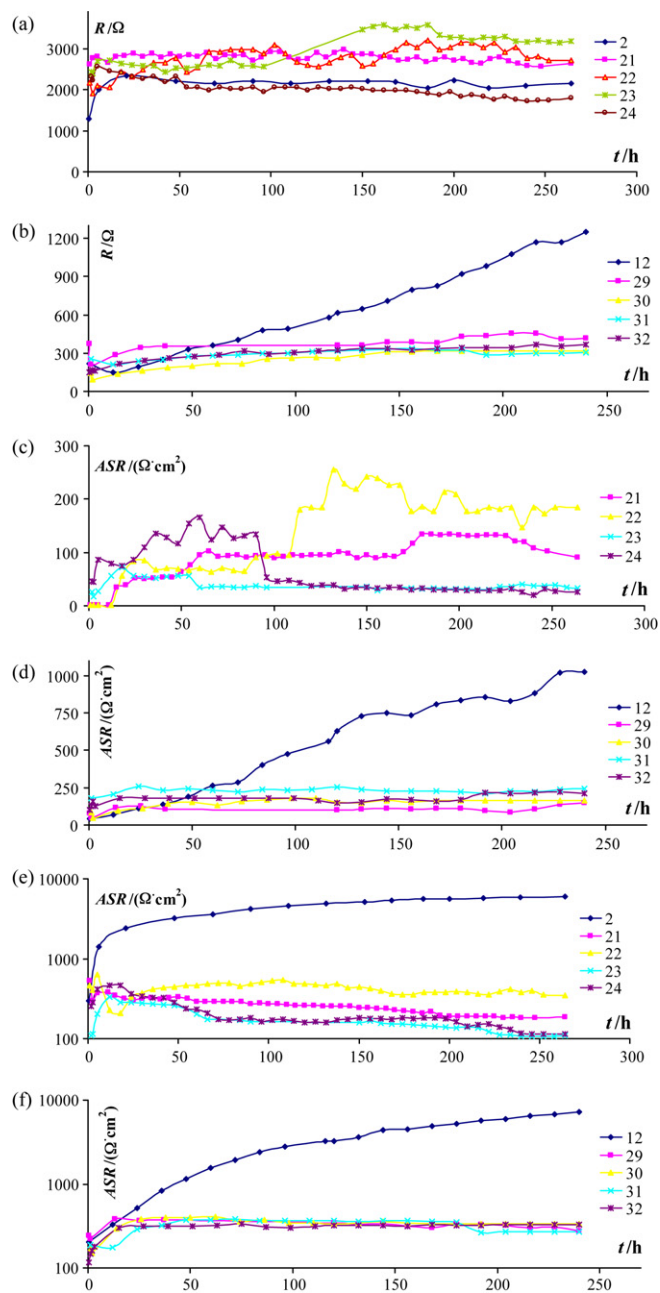


Fig. 5. Symmetric Li–Li cells' characteristics as a function of time: (a) L electrolytes' resistances, (b) S electrolytes' resistances, (c) charge transfer resistance for L samples, (d) charge transfer resistance for S samples, (e) lithium–electrolyte interfacial resistance for L samples, and (f) lithium–electrolyte interfacial resistance for S samples. Take care with the logarithmic scale in the interface resistance plots.

At temperatures above polymer melting point, temperature dependence of conductivity can be very well described by free-volume-theory [29–33]. Below this temperature dependence is Arrhenius-like, with a small kink located around 263 K (around 20 K below  $T_m$ ). VTF fitting<sup>3</sup> brought  $T_0$  values (Fig. 3) that

<sup>3</sup> Fitting data range was quite narrow and  $T_0$  values are quite low, but good quality conductivity data and precise temperature control resulted in  $(1-r^2)$  fitting values as low as  $10^{-5}$ . Moreover consistency in  $T_0$  values does not seem to be incidental.

are in good agreement with DSC data that can be found in literature [18], i.e. are ~30 K below  $T_g$  experimental values. It is interesting, that coarse fillers influence neither  $T_g$  nor  $T_0$  values, whereas nano-fillers caused  $T_0$  decrease. This fact needs to be confirmed by DSC (usually  $T_g$  changes are linked at least qualitatively with  $T_0$  changes).

On the other hand in case of PEO 4,000,000 based samples (S) no enhancement of conductivity was observed (Fig. 4). Furthermore, some lowering of its values was observed. This result from the fact, that during casting, larger grains fell down on the bottom of crystallizers and were acting as a blocking layer (see SEM micrographs). This was not observed in case of fine fillers. In liquid state (above  $T_m$ ) the lack of enhancement of conductivity is consistent with observations for L samples. But why there is no enhancement below  $T_m$ ? If one looks into the literature, it can be found, that thermal history of samples is of great importance and have major influence on the conductivity values [34,35]. Thus it is quite obvious to see, that L samples were stored for very long time (2 weeks or more) at tempera-

tures around 40 K above the  $T_m$ , whereas S samples were never kept above  $T_m$  before conductivity measurements. Some future work will be devoted to explain the influence of thermal history and cooling rates on the conductivity. Below  $T_m$  temperature dependence of conductivity is Arrhenius-like, with a small kink around 313 K (which is again around 20 K below  $T_m$ ).

### 3.3. Li transport number

Obtained transport number values are indicated in Table 2. It is clear, that addition of superacidic fillers increases readily the cation transference number [36]. This is in good agreement with what is stated in [35], that since movement of anions is coupled with segmental motions of polymeric chains and the latter is disturbed by inorganic fillers, their (fillers) addition increases the cation transference number in composite polymeric electrolytes. But this increase could be also caused by changes in charge carriers concentrations [37,38]. Further studies are required to explain this phenomenon.

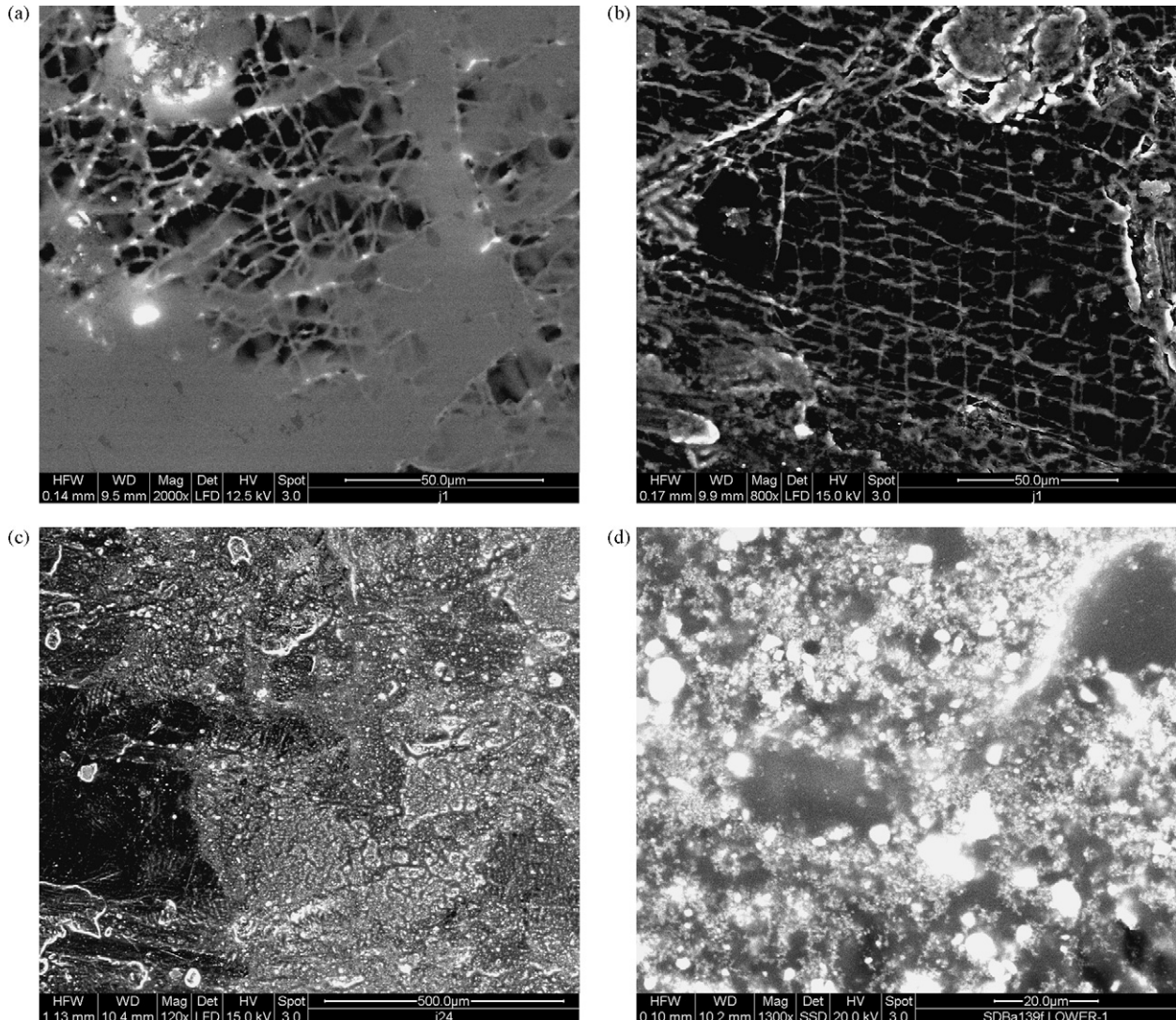


Fig. 6. SEM micrographs: (a) lithium surface covered with sample #1, (b) lithium surface covered with sample #2, (c) lithium surface covered with sample #24, (d) lithium surface covered with sample #24 (BSE detector), (e) cross-section of sample #30, (f) bottom side of sample #32, and (g) upper side of sample #32.

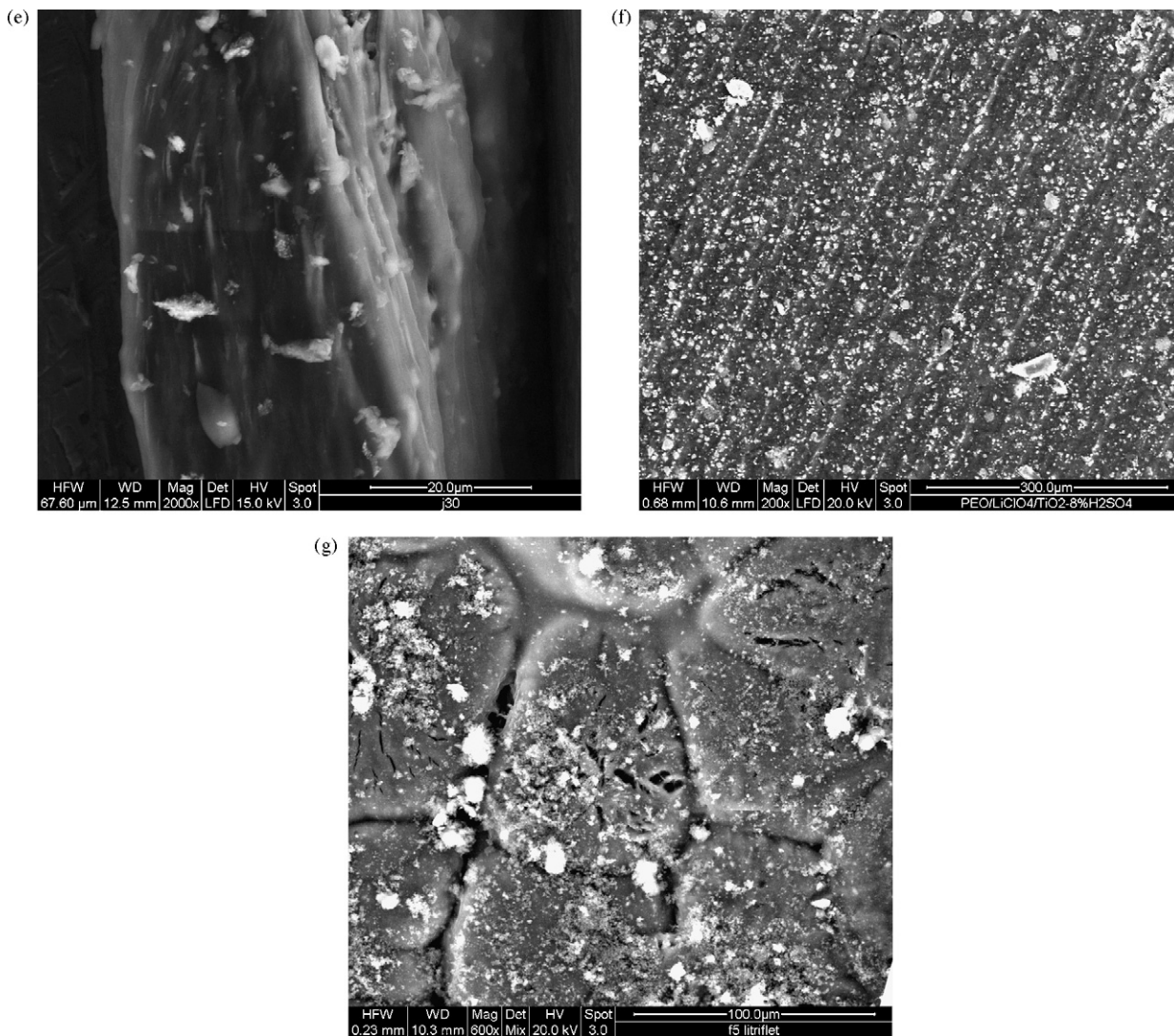


Fig. 6. (Continued).

The only strange thing is that for samples without fillers, the transference number increases sharply after the first polarisation. This puts a question mark on the reliability of data collected after the first polarisation. For composite samples nothing strange happens, apparent transference numbers remain stable in time.

### 3.4. Electrolytes stability

From (almost) each impedance spectrum, three resistance values were obtained [21] that correspond to: HF loop and is attributed to the electrolyte resistance, MF loop that is usually attributed to the charge transfer resistance and LF loop that is believed to represent the interface resistance. These values<sup>4</sup> are plotted in Fig. 5. It is easy to see, that addition of fillers has a dramatic influence on the stabilisation of the interfacial resis-

tance in case of both S and L samples. Plain polymer with salt (high and low molecular weight) while in contact with lithium metal, develops an interfacial layer, whose resistance is continuously increasing in time. When “inert” filler was added, this resistance stabilised very quickly at low values, independently of the acid content. It had been suggested in [17] that this stabilisation results from the sedimentation of powder inside the cell onto the lithium electrodes and in such a way a protective layer is produced that prevents this layer growth. But those data were obtained only for PEODME 500-based electrolytes with alumina particles (the same as used in this project). Herein it is shown, that the same effect is observed for solid samples, for which sedimentation does not seem to be possible. In [17], cells were turned upside down every day and it is suspected that once particles felt down onto one electrode, they remained there after turning the cell and were still protecting the electrode. In these experiments, some of the cells were turned upside down, some were left in vertical and some in horizontal position. The stabilising effect is very similar, whatever the configuration. Even strong mechanical shocks did not change anything in the results.

<sup>4</sup> There is no data concerning charge transfer resistance for sample #2 because the MF loop was not observed in any of the spectra recorded.

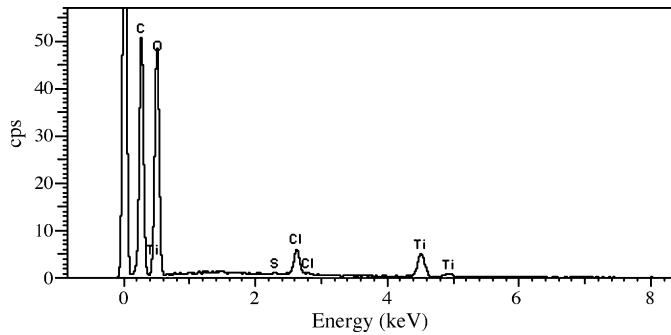


Fig. 7. X-ray energy-dispersive spectrum of sample #30.

This weird phenomenon needs much deeper investigations to be explained.

Within time frames of the project, only SEM observations were planned as the first attempt to explain what the reason of these amazing results was. Unfortunately these experiments have not given any clue on what is going on inside the cells. First of all great difficulties were encountered when trying to reach high magnifications because concentrated electron beam was destroying the polymer and thus changing the image during data collection. Anyhow, several pictures were taken and what was observed is that pure polymer develops quite uniform layer onto the lithium surface (Fig. 6a). Salt addition provokes some inhomogeneity in the surface appearance (Fig. 6b). Finally, addition of filler results in presence of its grains on the lithium surface (Fig. 6c and d) (picture taken with BSE detector clearly shows where the heaviest element (Ti) (and thus titania filler) is present on the surface).

Observation of foils themselves revealed several features. It appeared that sedimentation was taking place in slurries, during acetonitrile evaporation in crystallisers (Fig. 6e). As a result, upper part of every foil prepared (at least those with coarse fillers because only they were watched with SEM) was devoid of filler and the lower part was filler enriched. Grooves remaining on the crystallisers' bottoms after they are milled were imprinted on the bottoms of the foils (Fig. 6f). At the same time contraction joints were found on the top of every foil (Fig. 6g).

X-ray microanalysis (EDS) confirmed the electrolytes' compositions (Fig. 7).

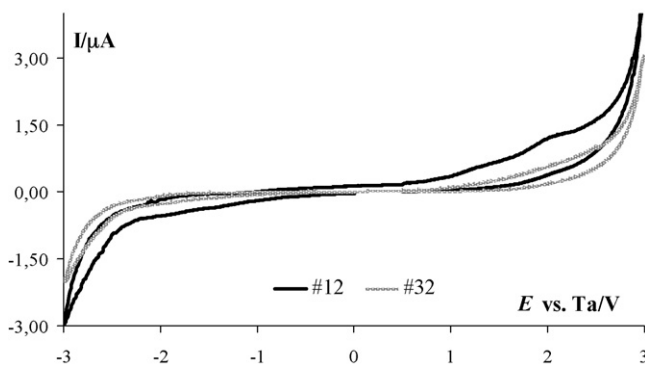


Fig. 8. Cyclic voltammograms of samples with (#32) and without filler (#12).

Cyclic voltammetry showed no influence of fillers on electrolytes stability (Fig. 8).

#### 4. Conclusions

Several conclusions can be drawn on the basis of these results. First of all—there is little impact of the filler on the conductivity of polymeric electrolytes (at least those studied here) above the polymer melting temperature. Conductivity below this temperature can be influenced by the filler significantly, provided that the electrolyte had been stored in liquid state before. Temperature dependence of conductivity can be described by two different equations (Arrhenius and VTF), suggesting the predominant conductivity mechanism depends on the electrolyte structure (that changes with temperature).

A major increase in Li transport number is a very promising fact, and this observation confirms previously reported results [36] based both on dc and EIS results.

CV with Pt WE revealed no influence of filler on the electrochemical stability of electrolytes. On the other hand, results from EIS measurements in Li–Li cells show that resistance of Li–polymer interface stabilizes at low values provided that filler is present, regardless the physical state of the electrolyte (liquid or solid). This shows that by using low cost additives, not only the transport properties of polymeric electrolytes can be enhanced but also interfacial properties, which is of great importance for future application in Li-cells.

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