



Ceramic-in-polymer versus polymer-in-ceramic polymeric electrolytes—A novel approach

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ABSTRACT

A new type of composites, i.e. polymer-in-ceramic (as opposed to the “classical” ceramic-in-polymer approach) was introduced into the field of composite polymeric electrolytes. In this work the preparation of porous ceramic samples based on alumina is designed and their properties are characterised by XRD, porosimetry and SEM. Special setup was developed for the preparation of electrolytes in vacuum/controlled atmosphere conditions and it was used for preparing the composites. The studied systems exhibited excellent mechanical properties, high conductivities and good stability vs. Li metal electrodes under prolonged storage.

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1. Introduction

The demand for the most efficient energy storage and conversion device results in the need for the development of cheap, reliable, durable and most of all environmentally-friendly batteries. They are crucial for the fulfilment of the greenhouse gasses emission goals and increasing the energy-flexibility of the future generations. The most promising and widely studied are lithium cells that offer highest energy densities and cell voltages among all battery systems known [1]. However environmental and safety issues prohibit production of large Li batteries in the present technology because of the liquid electrolytes inside. In order to bypass these issues the suggestion by Armand et al. of using solid polymer electrolytes [2] has been widely explored over last three decades. One of the cheapest, most environmentally-friendly and most promising materials are polymer-salt complexes based on Li salts and poly(ethylene oxide). The early studies on these complexes by Wright and co-workers [3] showed low room temperature conductivities. Further works on these materials were mostly devoted to enhancing the ion transport properties. However usually there has been a trade off between ionic transport and mechanical properties. In general rigid

structures that are interesting from the point of view of application in all-solid-state cells are characterised by low conductivities. That's one of the reasons why dry polymer electrolytes have not been applied in commercially available cells so far.

Coming into details, rather poor conductivities of plain salt-polymer mixtures resulting from large crystallinity of PEO and its complexes can be enhanced without any loss of mechanical properties [4] by introduction of ceramic fillers. Interactions between filler grains with the polymeric matrix were proven to be benefit for the properties of composites [5,6]. Confinement and entanglement of polymeric chains in the vicinity of the grains can propagate athwart the electrolyte and influence its conductivity, ion transference number, interfacial, mechanical and thermal properties.

Although the “classical” ceramic-in-polymer systems have been widely studied there is not too much information on inverse systems, that is to say polymer-in-ceramic ones. In the present work we have decided to study this type of composites—in which the ceramic is a continuous phase that provides mechanical support for the electrolyte and salt-polymer complex being soaked in it. This approach gives many opportunities and opens new ways of thinking about composite materials. It is quite sure that convex vs. concave neighbourhood of polymeric chains can differentiate properties of ceramic-in-polymer vs. polymer-in-ceramic polymeric electrolytes. Furthermore continuous ceramic phase enables new materials to be used as the ion-conducting phase since the mechanical integrity and rigidity of the system is assured by the ceramic phase.

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Limited studies have been carried out on layered ceramic precursors from silicate, hectorite and montmorillonite families into which molten high molecular weight PEO or low molecular weight organic solvents were incorporated together with the lithium conductive salt [7–10]. Improvement in the cation transference number in these materials compared to pure polymeric electrolytes has been reported [7]. Also these composites exhibited conductivities comparable to polymeric electrolytes used for their formation compromised with good mechanical stability. Based on our best knowledge none of the studies concentrated on the specially tailored architecture of the pores used as a ceramic skeleton for the electrolyte.

Such an unexplored area is interesting for the fundamental studies as well as from the application point of view. The idea is to divide the transport and mechanical properties into two separate phases, similarly to the Bellcore® technology [11], however here the conducting phase is meant to be polymer and not a volatile solvent, and the rigid phase is meant to be a porous ceramic that is compatible with electrode and electrolyte materials. Similar structures can be met in nature (for example bones, that are polymer (collagen) in ceramic (hydroxyapatite) structures).

One of the advantages of polymer-in-ceramic materials is their quasi-elasticity. Ceramic materials are usually sensitive to brittle cracking. When polymer and ceramic form interpenetrating, continuous phases and the polymer content is sufficiently high, the strain vs. stress graphs indicate some elasticity at high strains. This is very interesting from the application point of view because batteries can be exposed to large external forces. Possibility of avoiding a failure cannot be overvalued, especially in the case of large-scale, high-energy batteries where a failure can lead to fire and contamination.

In this paper we report a new class of ceramic composite polymer electrolytes where polymer-salt complex is permanently soaked inside the pores of a porous ceramic foil. First tests on the conductivity and electrochemical stability are provided as well as the synthesis route of ceramic sponge-like foils with desired porosity.

2. Experimental

2.1. Porous ceramic synthesis

Porous ceramic matrix was obtained via tape casting method with pore forming agent, by so-called organic additive (hereafter OA) burnout method, as well as without this additive by uni-axial (hereafter UA) pressing and grain sintering (hereafter GS). The number appearing after the UA and GS symbols stands for the average grain size of the powder used for the preparation expressed in micrometers (that rules the pore size).

Tape casting is a method of forming ceramic profiles of large surface area and small thickness (usually 0.05–2 mm). The use of pore forming agent enables high control of pore size and porosity. Besides it guaranties uniformity of pore distribution.

α -Al₂O₃ (A16SG, Alcoa) having a 0.5 μ m mean diameter grain size, density of 3.926 g cm⁻³ and specific surface measured by the BET method equal to 8.28 m² g⁻¹ was used for casting. The casting slip to prepare the tapes was processed by adding a defoculant (KD-1, hypermer, $d = 1.13$ g cm⁻³, ICI Europe Ltd. Belgium), binder (PVB 4000-2, poly(vinylbutaral), $d = 1.2$ g cm⁻³, Denki Kagaku Kogyo, Japan), plasticizer (*n*-butyl phthalate, $d = 1.043$ g cm⁻³, P.P.H. POCh, Gliwice). Azeotropic mixture of trichloroethylene and ethanol was used as the solvent for dispersion of ceramic particles. Concentration of solid in the slurry was 55.6 wt%. The mixing of the casting slip was conducted for 1.5 h in plastic mills with plastic-covered balls. Pore forming agent (microcellulose CC31 of average

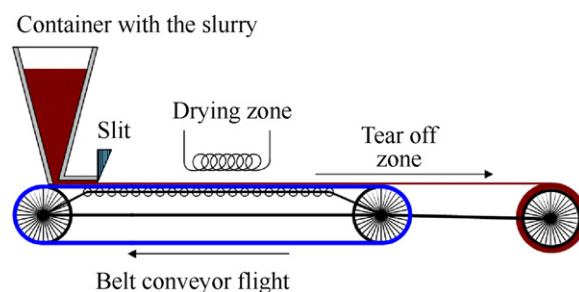


Fig. 1. Scheme of ceramic tapes forming process.

fibre length of 25–75 μ m, $d = 1.58$ g cm⁻³, Whatman International Ltd.) was added to the slurry and it was subsequently mixed for another 15 min in planetary ball mill.

Scheme of forming process can be described in Fig. 1. Ceramic slurry is poured onto the carrier surface covered with a hydrophobic polyester tape. The height of ceramic slurry layer is determined by height of the gap between surface carrier and calibration knife (500 μ m). After the green tape was dried for 24 h at room temperature, circle samples of 11 mm diameter were cut out. In order to obtain samples of desired height circle samples were laminated under high pressure in steel moulds by means of hydraulic press. Laminated samples were sintered for 1 h at 1550 °C in air.

The UA0.5 samples were prepared by uniaxial pressing at 50 MPa in a steel matrix. Powder was the same as in case of OA samples. As a binder an excess of poly(vinyl alcohol) was used. Degree of hydrolysis was 88%, average molecular weight 31,000 Da. Green pellets were fired at 1200 °C in air.

The GS50, GS65 and GS80 samples were prepared by the grain sintering method. This is one of the easiest and most popular method allowing obtaining open and transient pores. However the maximum porosities usually do not exceed 50%. Pore size depends directly on the initial grain size. Powder was α -Al₂O₃ obtained from POCh Gliwice, separated into fractions by sieving. As a binder an excess of aqueous solution of carboxymethylcellulose (Loba-Chemie, Austria) was used. Samples were pressed uniaxially at 10 MPa and fired at 1500 °C in air.

Samples showed average linear shrinkage of 13.55 \pm 1.85%. After polishing by means of silicon carbide powder, basic physical parameters, such as open porosity (P_o), apparent (d_v) and relative density (d_r), water absorption capacity (N), were measured by means of hydrostatic method (Table 1).

2.2. SEM instrumentation

The morphology and surface properties of samples were examined by Quanta 200 Scanning Electron Microscope with EDS analyzer (FEI). The accelerating voltage was 15(20) kV and spot size 3.5(4.0). Pictures were taken under low vacuum of 60 Pa conditions. Samples were not subjected of any conducting coating vacuum deposition pre-treatment.

2.3. Composite electrolytes synthesis

Poly(ethylene oxide) dimethyl ether, average molecular weight 500 g mol⁻¹ (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

Table 1
Basic physical parameters of sintered ceramic bodies (OA method).

P_o [%]	N [%]	d_v [g cm ⁻³]	d_r [%]
48.46 \pm 1.69	23.76 \pm 1.64	2.04 \pm 0.08	52.06 \pm 2.15

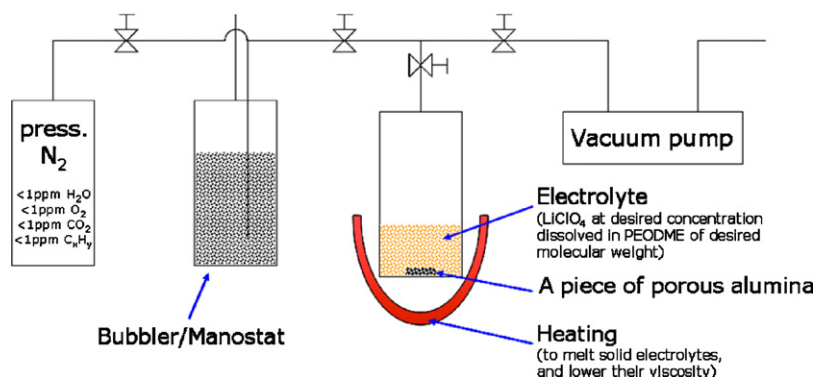


Fig. 2. Experimental setup used for the composite electrolytes preparation.

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) dimethyl ether, average molecular weight 1000 g mol^{-1} (PEODME 1000, Sigma–Aldrich) that is solid at RT was dried in a vacuum line, first at RT for 24 h and then at 353 K for 72 h (in the melted form). Dry PEODME 1000 was transferred under vacuum to the dry-box where it was used. LiClO_4 (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 393 K for 72 h. Dry LiClO_4 was transferred under vacuum to the dry-box where it was used. Porous ceramic pieces were dried at RT for 24 h and then at 423 K for 72 h. They were transferred to the dry-box under vacuum afterwards. In all cases pressure was kept below 5×10^{-10} bar.

To prepare composite polymer electrolytes, soaking of ceramic in a polymer melt mixture under vacuum was chosen as a method of preparation. It was necessary to avoid any contact with air (moisture, nitrogen, oxygen, carbon dioxide) therefore transfer of the components between the vacuum line and the dry-box was always under vacuum. The scheme of the experimental setup is given in Fig. 2.

At first electrolytes solutions –1 and 2 mol kg^{-1} LiClO_4 in both 500 and 1000 g mol^{-1} PEODME were prepared inside the dry-box. Dissolution of the salt into the polymers was conducted on a magnetic stirrer at 323 K. At this temperature both polymers are liquid. Once the solutions were ready, porous ceramic pieces of known weight were put inside vials with electrolyte solutions, this was put into a vacuum vessel and as such connected to the vacuum line where argon was pumped out from the vessel. Its temperature was then raised up to 380–390 K in order to melt the electrolyte and lower its viscosity. On pumping argon was removed from the pores what could be observed in a form of bubbles. Once bubbling stopped (~ 3 h) the vacuum pump was disconnected and the vessel was filled with pure nitrogen. Since the ceramic piece was sunk in the liquid electrolyte, the nitrogen pressure drove the liquid electrolyte in. The pumping–nitrogen filling was repeated, third pumping followed and then the vacuum vessel was transferred back to the dry-box where vial was placed on a hot plate (330 K) and the soaking with electrolyte solution could proceed in pure argon for a day. After cooling the composite down to RT the excess of the electrolyte was carefully removed from the surface and the sample's weight was checked in order to verify if the soaking was complete. Such composites did not exhibit any propensity to electrolyte efflux regardless the molecular weight of the polymer.

2.4. Electrochemical studies

Conductivity measurements were made using complex impedance method [12] in a wide temperature and frequency

range. Samples were put between stainless steel blocking electrodes in Swagelok cells and their impedance was measured using computer-interfaced VMP3 Multichannel Potentiostat–Galvanostat (Biologic Science Instruments), in 500 kHz–1.00 MHz frequency range with 20 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.

The electrochemical characterization of lithium–electrolyte interface was studied using VMP3 Multichannel Potentiostat (Biologic Science Instruments) by recording impedance spectra in 500 kHz–1 MHz frequency range with 20 mV signal amplitude. Symmetric Li–Li cells were prepared in Swagelok cells. Li metal discs (400 μm thick, Sigma–Aldrich) were sandwiched on both sides of the electrolyte and this stack was placed between stainless steel current collectors. Since temperature has a great influence on the impedances of these electrolytes, their evolution was examined in temperature-controlled environment. Cells were put in an oven set at 310 K. Evolution of the impedance was examined by recording impedance spectra day by day for up to 70 days.

3. Results

3.1. Porous ceramic characterization

Fig. 3a and b depicts scanning electron micrographs of a surface and cross-section morphology of the obtained porous ceramic samples before soaking with the electrolyte solution. The SEM images generally display a continuously porous but uniform surface. As desired there is no significant non-uniformity of the pores between the surface and cross image of the samples. Those with 60% porosity consist of large (5–100 μm), featureless agglomerates, which are fused together into a micro- and nano-porous “lava rock”-like structure. The 35% porous material exhibits more consistent and solid morphology without tendency of agglomeration. SEM studies confirm the correlation between size of the initial grain and architecture of the pores but both materials show high constant average size of free volume between ceramic grains.

Apart from that several engineering improvements are still under consideration for our future work. We suspect that better control and/or design of pores architecture is crucial to assure further improvements of physicochemical properties of the final electrolytes.

3.2. Composite electrolytes

3.2.1. Conductivity studies

Impedance spectra of SS|CPE|SS cells consisted of a high frequency semicircle with a low frequency spike. They were fitted with *Equivalent Circuit by Boukamp*TM [13,14]. The semicircles were

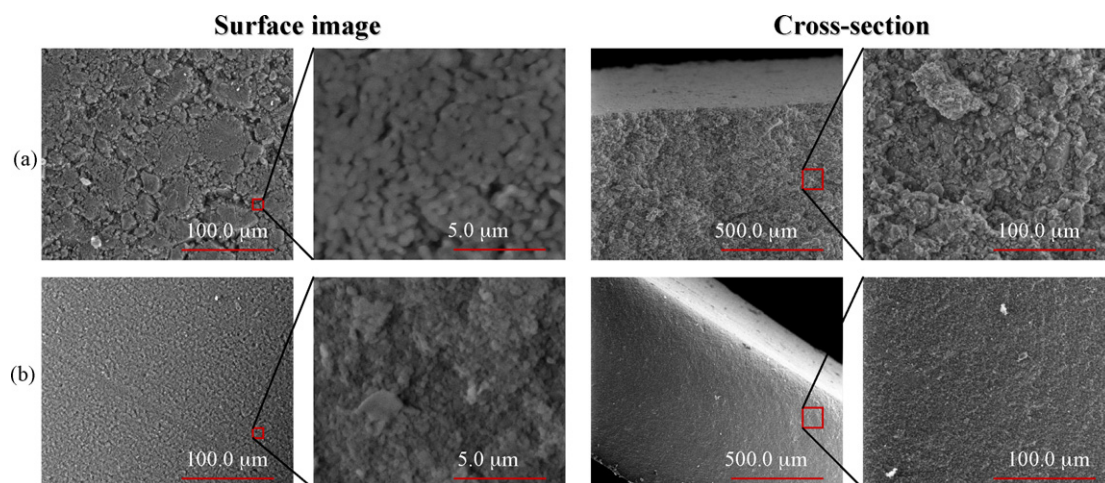


Fig. 3. SEM images of ceramic samples obtained from (a) 65 μm powder (with 60% porosity) GS65; (b) 0.5 μm powder (with 35% porosity) UA0.5.

clearly of single resistor (R), constant phase element (Q) origin. Furthermore values of the “ n ” parameter, standing for the deviation of the constant phase element from a capacitor (that usually describes non-uniformity of the system under study) used to be very close to unity suggesting that samples were rather uniform. No additional features were observed that could result from interfacial layers (no evidence of leaks).

In Fig. 4a–e the results of the conductivity measurements are presented. Logarithm of the conductivity as a function of reciprocal temperature is plotted. Squares correspond to PEODME500-based electrolytes, whereas triangles to PEODME1000-based ones. Lines are plotted as guides for the eyes.

3.2.2. Stability studies

AC impedance studies on these composite electrolytes made at 310 K showed good stabilities vs. Li metal electrode. In many cases all the equivalent circuit elements corresponding to the electrolyte (high frequency), charge transfer (medium frequency) and interfacial resistance (low frequency) remained stable in time, however in some cases they were increasing over the storage time. Values of the interfacial resistance are plotted in Fig. 5a–d. The exemplary cole–cole plot is given in Fig. 6 together with characteristic frequencies as well as capacities of corresponding capacitors (C) and constant phase elements (Q). The interpretation of our spectra is quite similar to the one given by Zhang et al. in [15].

4. Discussion

4.1. Conductivity

Several key factors influencing the conductivity were studied: the molecular weight of the polymer, salt concentration, porosity, pore architecture and the pore size. First of all increase of the molecular weight causes conductivity drops. This conclusion is common for all the samples (Fig. 4a–e). The product of remaining factors is usually not easy to foresee. In general composites exhibited lower conductivities than their non-composite counterparts at temperatures above the polymer melting point and enhanced transport properties below this temperature.

The most spectacular example of enhancement of conductivity is that of the 2 M LiClO_4 in PEODME 1000 soaked into the porous ceramic obtained by the organic additive burnout method that exhibited the largest pore size resembling the size of the cellulose fibres (Fig. 4a). In this case RT conductivity of $10^{-5} \text{ S cm}^{-1}$ was

reached for a dry solid polymeric electrolyte. Such high conductivities were not observed in any other sample based on the heavier oligomer. On the other hand the crystallisation of such a viscous electrolyte is quite slow provided that there are not too many crystallisation centres. In fact, almost unfaulted VTF conductivity vs. temperature profile supports the hypothesis of seriously inhibited crystallisation of this electrolyte.

As observed visually the crystallisation of all the other electrolyte solutions was much faster. These electrolytes exhibited higher conductivities when soaked in porous alumina samples obtained by the grain sintering (Fig. 4b–d) and uniaxial pressing methods (Fig. 4e). In a few cases conductivities of composites slightly exceeded those of base electrolytes, however usually there was a minor drop in conductivity above the polymer melting point. This is especially interesting because in case of alumina with 50% porosity, the weight fraction of the non-conductive ceramic phase exceeds 75%. In case of “classical” ceramic-in-polymer electrolytes, the filler weight fraction is usually 10%.

Nevertheless the temperature zone, where the beneficial influence of the ceramic matrix on the conductivity can be clearly seen, is below the polymer melting point. The PEODME500-based samples soaked into the coarse-grained-based porous ceramic samples exhibited a major increase of the conductivity at sub-ambient temperatures as compared to the non-composite ones. In the case of the 2 M solution in the $\sim 50 \mu\text{m}$ grain sample there was no evidence of crystallisation and the conductivity vs. temperature plot preserved its “VTF” shape below the polymer melting point (Fig. 4d). The same behaviour was observed in the case of 0.5 μm grain ceramics, but here even 1 M sample behaved in a similar manner (Fig. 4e). In general all the PEODME500-based samples’ transport properties were significantly enhanced in sub-ambient temperature zone by the presence of the ceramic matrix. Sometimes slight kinks of the conductivity vs. temperature profiles were observed at the melting point but often only slightly pronounced or even no transition was observed on cooling when passing the polymer melting point.

To sum up, first results suggest that best conductivities are obtained for small pores and low molecular weight of the polymer. In case of high molecular weights larger pores are more desired, especially when the salt concentration is high.

4.2. Stability studies

AC impedance studies on these composite electrolytes conducted at 310 K showed good stabilities vs. Li metal electrode. In most cases all the equivalent circuit elements corresponding

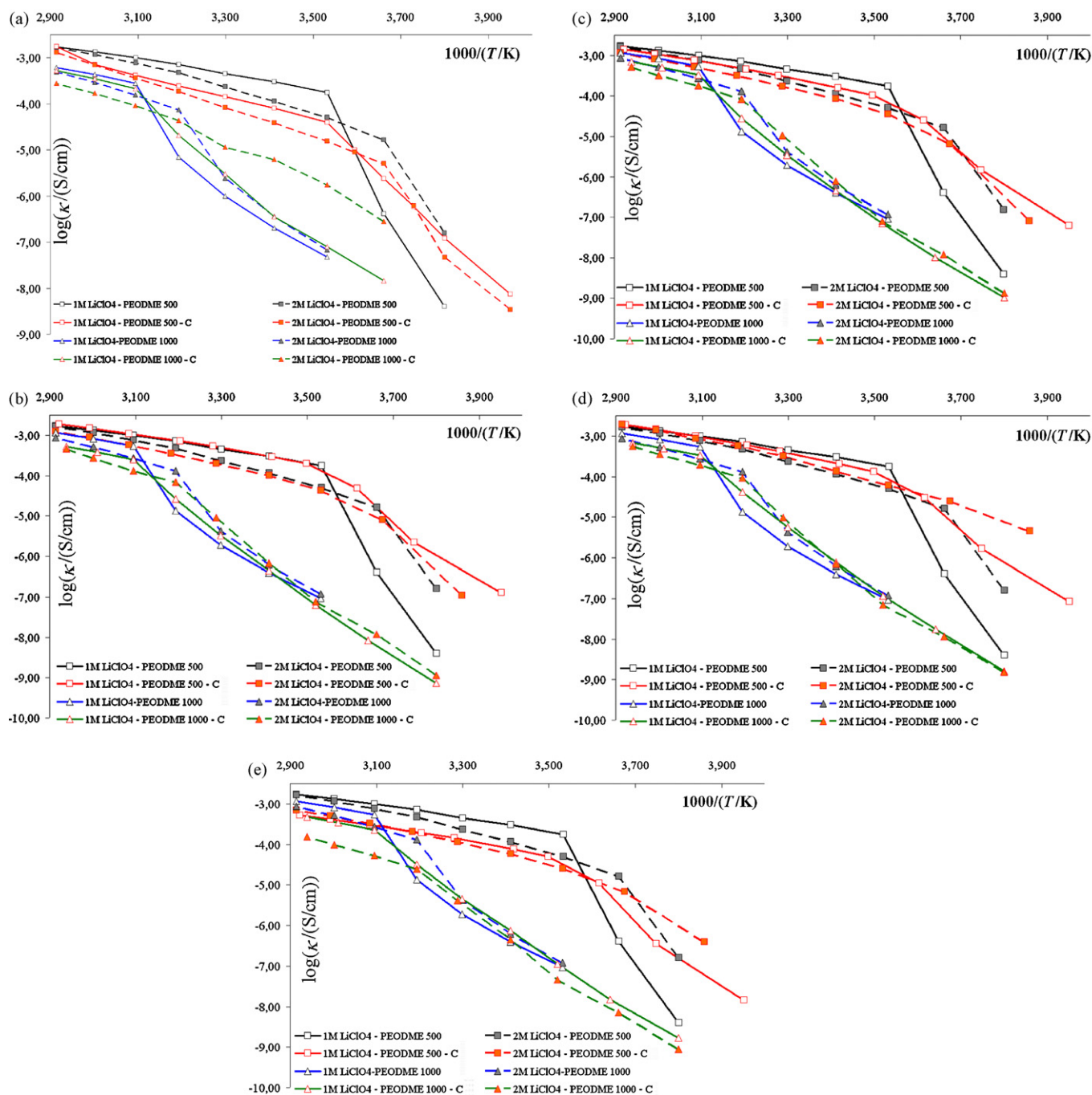


Fig. 4. Conductivity vs. temperature profiles. "C" indicates composite samples. (a) OA ceramic, 25–75 μm cellulose fibres, 0.5 μm alumina grains, 50% open porosity; (b) GS ceramic, 80 μm alumina grains, 60% open porosity; (c) GS ceramic, 65 μm alumina grains, 60% open porosity; (d) GS ceramic, 50 μm alumina grains, 60% open porosity; (e) UA ceramic, 0.5 μm alumina grains, 35% open porosity.

to the electrolyte (high frequency), charge transfer (medium frequency) and interfacial resistance (low frequency) remained stable in time, however in some cases they were increasing over the storage time (Fig. 5a–d). Our suggestion is that the air tightness of these cells was not perfect. Opening the cells revealed light grey surface of lithium electrodes in the case of stable cells and some dark deposits (possibly Li_3N) in the case of cells that failed. The lithium nitride could be a product of reaction with nitrogen coming into the samples from the air. At the same time the stable behaviour of most of the cells suggests that nitrogen used at the vacuum line to drive the electrolyte into the ceramic pieces did not dissolve excessively in the solution and was not an issue for the stability against lithium metal. In general the interfacial

resistance increases with the polymer molecular weight supporting the idea that the polyether-based electrolyte–lithium metal interface is mainly built up by the polymer and thus its transport abilities determine in certain extent the interfacial resistance. For PEODME500-based samples the interfacial resistance was the same for both 1 M and 2 M solutions, whereas for PEODME1000-based samples, interfacial resistances were c.a. three times lower for the 2 M solution than for the 1 M one. All the samples seem to be capable of exhibiting good stabilities vs. Li metal electrode however the experimental conditions can influence the results (air tightness of the cells). This way or another better stabilities were obtained for samples with larger pores and larger porosities.

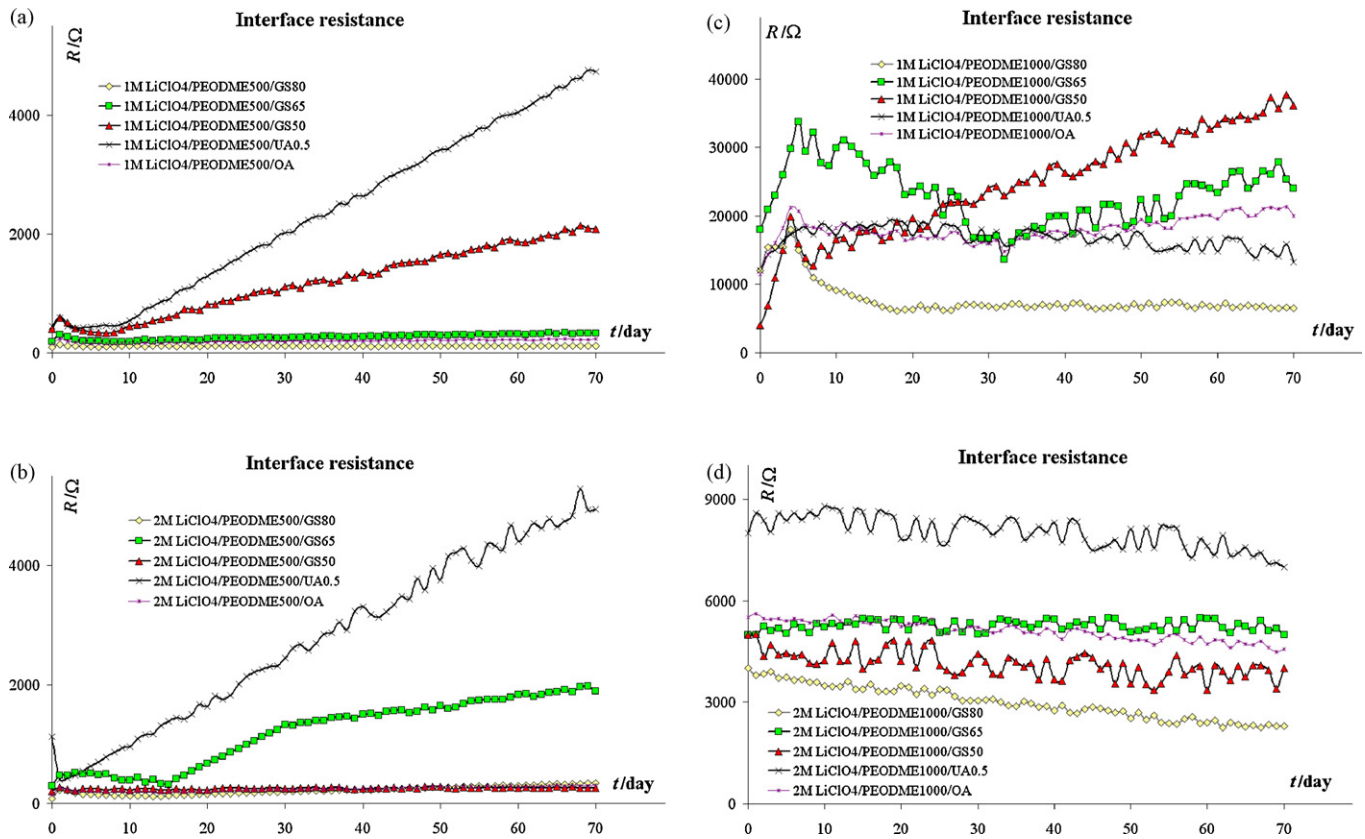


Fig. 5. Evolution of the interface resistance of Li metal-composite electrolytes based on: (a) 1 M LiClO₄/PEODME500; (b) 2 M LiClO₄/PEODME500; (c) 1 M LiClO₄/PEODME1000; (d) 2 M LiClO₄/PEODME1000.

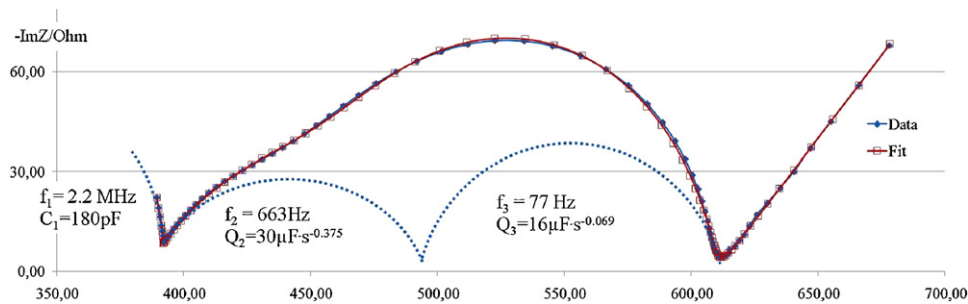


Fig. 6. A typical cole-cole plot obtained on Li-electrolyte-Li cell after several days of storage. Experimental data are plotted together with the fit and schematic representation of consecutive sub-circuits (their characteristic frequencies and capacitors/constant phase element parameters are given).

The first attempts of preparing polymer-in-ceramic composite electrolytes revealed great opportunities of reaching high conductivities in extremely rigid, leak-free samples. Optimisation of these systems is a subject to further studies. That shall consist in controlling the porosity, pore size, tortuousness and possibly the modification of the internal surface of the pores. That could lead to increased conductivities, better stabilities of the Li-electrolyte interface [6] or even to increased Li transport numbers [16].

5. Conclusions

New class of composite polymer electrolyte material have been synthesized and preliminary tested. Electrolytes consisted of polymer electrolytes soaked inside the specially designed ceramic porous sponge-like material. First results executively confirmed two crucial factors deciding on the properties of whole composite system, e.g. porosity of the ceramic material and polymer matrix used in the electrolyte solution. Highest conductivities have been

obtained for sample 60% open porosity filled with PEODME500 1 M lithium perchlorate solution. All materials exhibited long term high stability towards lithium metal electrode.

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