Preparation and characterization of hot-pressed Li\textsuperscript{+} ion conducting PEO composite electrolytes

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Preparation and characterization of hot-pressed Li\textsuperscript{+} ion conducting Polyethylene oxide (PEO) composite electrolytes are discussed in this paper. Lithium trifluoromethanesulfonate with linear formula CF\textsubscript{3}SO\textsubscript{3}Li is selected as Li\textsuperscript{+} ion source for polymer composite electrolyte processing. Polyethylene oxide as matrix for polymer electrolyte is selected, because of its cation solvatation and salt complexes formation partibility. Nano-sized fillers such as carbon nanotube (CNT) and graphene (GR) are introduced to polymeric composite to improve PEO electrolyte mechanical properties. The composites were prepared from PEO, CF\textsubscript{3}SO\textsubscript{3}Li, CNT and GR by solution casting and by hot-pressing method. Influence of CF\textsubscript{3}SO\textsubscript{3}Li, CNT and GR concentrations on the electrical, thermal and mechanical properties of PEO composite is investigated and discussed. The additives addition to the PEO matrix improves the electrical, thermal and mechanical properties of the composite. The crystallinity of the PEO decreases.

1. Introduction
The term “battery” describes a device that converts the chemical energy contained in its active materials directly into electric energy through the electrolyte, which provides the essential ionic transfer [1-3]. Wide range of film-like solid polymer electrolyte designs are already utilized in batteries, mostly in portative electronics because of light-weight, non-toxicity, non-combustibility, easy forming, mechanical stability [1,3-9]. For the solid polymer electrolyte system it is important that polymer has a strong coordination to the cations. Polyethylene oxide (PEO) have no double bonds and have a “plenty” of space between its oxygen groups, which is preferable for many different types of cation solvatation and salt complexes formation [3,8-10]. Nuclear magnetic resonance spectroscopy results of PEO-Lithium salt systems show that conductivity is dominated by the movement of lithium ion, i.e., the lithium transport number is 1.0 [11]. Melting temperature “T\textsubscript{m}” of the polymers is one of the most important technological parameters, because all processes and practical application of ready material are highly affected by it [12]. Differential scanning calorimetry (DSC) results indicate that addition of Lithium salt decrease important melting values, such as degree of crystallinity and melting temperatures [2,13]. It can be concluded, that increasing the amorphous phase amount and mobility of Lithium cations could increase the ionic conductivity of polymer electrolyte [1,10]. At the same time, the limit of conductivity for applications is 10\textsuperscript{-5} S/cm (in the range between 20°C and 100°C). The limit for conductivity to amorphous phase is its glass transition temperature, but no higher than it. Some authors claim, that ionic conductivity in solid PEO-Lithium salt system reached averaged maximum 10\textsuperscript{-6} S/cm [2,14,15]. However, ionic conductivity of PEO-alkali metal...
salt system was reached $10^{-7}$ S/cm at room temperature. PEO-Lithium salt system were revealed to be amorphous when the molecular weight was in range 300-750 g/mol, but system that was obtained with PEO higher than 1000 g/mol - partly crystallized [16]. This phenomenon is based in decrease of crystallite size, which occurs at higher PEO molecular weight, although it cannot explain the different activation energies in the systems [17]. PEO-Lithium salt systems show highest conductivity with PEO molecular weight value lower than 300 000 g/mol.

Lithium trifluoromethanesulfonate (LiTrifl) with linear formula CF$_3$SO$_3$Li is widely used as ion source and plasticizer [2,3,8-11,13-19]. The Lithium ion is the stronger Lewis base of the group. It accepts the lone pairs on oxygen the quickest and easiest and has the highest relative exposed positive charge. Hence it will attract water, making the salts hygroscopic and therefore more flexible [20]. Hydrates still exist in Lithium salts after 12 h of drying at 300°C [21,22]. LiTrifl start its decomposition at 290°-300°C [15,23]. Aim of nano-filler addition is the reducing the crystallizing ability of the polymer without reducing the mechanical properties of the PEO composite. The carbon nanoparticles network-polymer composite exhibits electron tunneling conductivity, which show that the CNTs and GRs network offers a promising application as filler material for creating super conductive composite [15,24-26].

The aim of this paper is to explore LiTrifl salt concentration effect on electrical conductivity and thermal properties of hot-pressed Li$^+$ ion conducting PEO composite electrolytes.

2. Methodology

2.1. Sample preparations

PEO was chosen as matrix of composite polymer electrolyte. LiTrifl as ion source. As reinforcing additives were chosen: CNT and GR. Properties of substance given above were supplied by manufacturer and are listed in table 1.

| Substance | Manufacturer       | Substance properties                                      |
|-----------|--------------------|----------------------------------------------------------|
| PEO       | Scientific Polymer Products | MW. 100 000 g/mol; relative d = 1.21 g/cm$^3$; Tm = 65°C |
| LiTrifl   | Fluorochem         | MW 156.01 g/mol                                           |
| CNT       | Nanocyl$^{TM}$ NC 7000 (multiwall) | relative d = 1.3-2 g/cm$^3$; E = 1TPA, $\sigma_B$ =10-60 GPa, $\varepsilon_B$ = 10% thermal conductivity, $>3000$ W/m·K $\sigma$ =10$^6$-$10^7$ Sm/m; average D = 9.5 nm, average L = 1.5 μm |
| GR        | XGNp Sciences      | relative d = 2.2 g/cm$^3$; E(||)=1GPa; $\sigma_B$(||)=5 GPa thermal conductivity (||), $>3000$ W/m·K $\sigma$ =10$^6$-$10^7$ Sm/m; average thickness = 7.5 nm average surface area = 120…150 m$^2$/g |

6% PEO solution was prepared by dissolving PEO in dimethylformamide (DMF) and mixed with magnetic stirrer at 70°C (20 min). LiTrifl, CNT and GR were dispersed in DMF by ultrasound for 5 min. It was added to 6% PEO solution and dispersed with additional ultrasound for 10 minutes. The polymer solution was casted as film and solvent was allowed to evaporate for 24 h at 45°C with subsequent annealing in vacuum at 45°C for 24 h. Films with average 500 μm thickness were prepared in mold at 90°C (6 min) by heat-pressing equipment. Concentrations of CNT and GR in composite were 0.05, 0.01, 0.25, 0.50 % of dry PEO mass. Two different system of LiTrifl concentration were separately studied, for CNT: 5, 15, 25% and for GR: 0.5, 1.5, 2.5% of dry PEO mass.

2.2. Volume resistivity measurements

The electrical conductivity of the sample was measured by sandwiching the samples between 2 electrodes using “Keithley 6487” picoampermeter. Constant 500V voltage for 60 s at 23°C was applied. Direct
current conductivity measurements were made. Root mean square errors for obtained data were calculated, which are less than 5% for all samples with two parallel measurement. The resistivity to the flow of current through a material is known as volume resistivity ($R_V$). Specific volume resistance ($\rho_V$) for the thin sample should be calculated using the following equation (1):

$$\rho_V = R_v \cdot \frac{22.9 \text{cm}^2}{h}, \Omega \cdot \text{cm}$$

(1)

$R_v$ – measured volume resistance of the sample (V/I), [Ω]; $h$ – thickness of the sample, [cm]; 22.9 – surface area of the electrode, [cm²].

2.3. Differential Scanning Calorimetry

Thermal analysis was performed on “Mettler Toledo DSC30” equipment at heating and cooling rates of 10°C/min from 20°C to 100°C under a N₂ atmosphere. It is known, that completely (100%) crystalline PEO polymer melting enthalpy ($\Delta H^°$) is equal to 213.7 J/g [6,7]. Using the equation (2) from below, we can calculate degree of crystallinity of PEO composite samples:

$$\chi = \frac{\Delta H_m}{\Delta H^°_m} \cdot 100\%$$

(2)

$\chi$ – degree of crystallinity of sample, [%]; $\Delta H_m$ – melting enthalpy of sample, [J/g]; $\Delta H^°_m$ – completely (100%) crystalline PEO polymer melting enthalpy, [J/g]

2.4. Mechanical properties

Mechanical testing was performed using a computer-controlled micro-force tester “ZWICK BDO-FB 020TN”. The composite film sample in the form of film “dogbone” strip (20mm x 5 mm). The speed for the elongation test was maintained at 5 mm/min at 23°C.

3. Results and discussions

3.1. Conductivity measurements

Calculated electrical conductivity from specific volume resistance is summarized in figure 1, 2 and 3.

Conductivity results (figure 1) of the PEO/CNT and PEO/GR composite show, that addition of 0.05% GR increase conductivity of pure PEO from $7.8 \cdot 10^{-12}$ S/cm to $82.4 \cdot 10^{-12}$ S/cm. It can be concluded, that addition of only 0.05% GR increase conductivity of pure PEO by 10 times. At the same time, the opposite situation is with addition of 0.05% CNT, because conductivity decreased by 18 times from $7.8 \cdot 10^{-12}$ S/cm to $0.42 \cdot 10^{-12}$ S/cm. This behaviour can be explain by crystallinity degree increase and decrease of free Li⁺ ion mobility. It has been noticed in figure 1 that the conductivity decreases with the increasing content of filler in the range of 0.1% to 0.25%. However, the conductivity start increase when the percentage of CNT and GR keeps on increasing.

Conductivity results (figure 2) of the PEO/CNT/LiTrifl composites show, that addition of LiTrifl increase electrical conductivity in all PEO/CNT/LiTrifl composites cases. Addition of 5% LiTrifl increase electrical conductivity of pure PEO from $7.8 \cdot 10^{-12}$ S/cm to $54.3 \cdot 10^{-12}$ S/cm (by 7 times), addition of 15% LiTrifl to $40.9 \cdot 10^{-12}$ S/cm (by 5 times) and addition of 25% LiTrifl to $32.8 \cdot 10^{-12}$ S/cm (by 4 times).
It has been noticed in Fig.2 that the conductivity of PEO/CNT/LiTrifl composites raises with the increasing content of CNT in the range of 0.1% to 0.25%. As it was mentioned in literature [27,28], the presence of CNT and GR nanoparticles enhances the electric conductivity substantially. It can be assumed that increase in the conductivity occurs as a result of filler addition, possible amorphous phase increase free Li\(^+\) ion higher mobility.

Similar behavior of electrical conductivity properties of PEO/GR/LiTrifl (figure 3) was observed before in PEO/CNT/LiTrifl composites. Addition of LiTrifl increase electrical conductivity in all PEO/GR/LiTrifl composites cases. Addition of 0.5% LiTrifl increase electrical conductivity of pure PEO from 7.8·10\(^{-12}\) S/cm to 99·10\(^{-12}\) S/cm (by 13 times), addition of 1.5% LiTrifl to 273·10\(^{-12}\) S/cm (by 35 times) and addition of 2.5% LiTrifl to 571·10\(^{-12}\) S/cm (by 73 times). Observed conduction behaviour could be attributed to higher contact surface of GR. It has been noticed in figure 3 that conductivity of PEO/CNT/LiTrifl with 0.5% and 2.5% LiTrifl content raises with the increasing content of CNT in the range of 0.05% to 0.5%, but decreases with 1.5% LiTrifl content in the range of 0.05% to 0.25%, however further addition of salt raise electrical conductivity.

### 3.2. DSC results

Results obtained in DSC are summarized in figure 4, 5 and 6. It consists of melting temperatures and degree of crystallinities values. We have tested the lowest and the highest content of the CNT and GR filler to see the main characteristic changes in polymer composite electrolyte thermal properties. Conductivity measurements also concluded the provisional relative changes.
PEO, decrease melting temperature from 66.7°C by 0.5°C and 0.8°C respectively. But addition of 0.5% CNT to PEO increase its melting temperature by 1.2°C, therefore electrical conductivity in this case decreased.

Figure 5 and figure 6 results show, that addition of LiTrifl decrease melting temperature and crystallinity in both of PEO/CNT/LiTrifl and PEO/GR/LiTrifl composite electrolyte systems. It should be noted, that addition of LiTrifl decrease melting temperature of PEO/0.05%CNT/LiTrifl composite from 66.2°C to 60.2°C, but addition of LiTrifl to PEO/0.5%CNT/LiTrifl decreased $T_m$ only to 60.8°C (figure 5), further addition of LiTrifl increase melting temperature. From figure 5 the minimal melting temperature corresponds to PEO/0.05%CNT/25%LiTrifl.

Meanwhile, it also can be observed in the figure 6, that addition of LiTrifl decrease melting temperature of PEO/0.05%GR/LiTrifl composite from 65.9°C to 62.1°C, but addition of salt to PEO/0.5%GR/LiTrifl decrease it only to 63.4°C. Bulk PEO melting temperature is lower than PEO film melting temperature. The difference between bulk ($T_m=65°C$) and film ($T_m=66.7°C$) PEO melting temperatures is equal to 1.7°C. We can suggest that this difference exist because of free volume theory and kinetic theory for structural relaxation, where dynamic displacements in film are higher than in bulk polymer [29,30].

### 3.3. Tensile strength properties

Concluding, we have tested tensile strength properties of PEO composite solid electrolyte samples.

Figure 7 results show, that pure PEO Young’s module is 357 MPa, but addition of CNT or GR reduce it up to 0.1% nano-filler content, further addition of CNT or GR increase module values. It is observed, that composite Young’s module values is higher in PEO/CNT case than in PEO/GR. In example, in PEO/0.1%GR composite Young’s module is equal to 293 MPa, but in PEO/0.1%CNT it is equal to 323
MPa, therefore it increased by 9%. Addition of 0.25% CNT to PEO/CNT samples increase Young’s module by 21%.

Figure 8 and figure 9 results show, that the higher amount of LiTrifl in both PEO/CNT/LiTrifl and PEO/GR/LiTrifl composite, the lowest Young’s module values obtained. Such a change in module values can be explained by the decreasing in crystallinity and increasing the amorphous phase by Li⁺ ion intercalation between polymer chains, therefore samples become more elastic. Figure 8 results show, that addition of LiTrifl to PEO/CNT/LiTrifl decrease Young’s module compare to PEO/CNT composite.

At the same time, figure 9 results show that addition of LiTrifl to PEO/GR/LiTrifl increase Young’s module compare to PEO/GR composite electrolyte. As the exception in PEO/GR/LiTrifl system, it was observed, that addition of 0.5% GR to PEO/2.5%LiTrifl composite decrease its Young’s module by 68% (figure 9). It was concluded (from figure 9), that the highest Young’s module of PEO/GR/LiTrifl system is for PEO/0.5%GR/0.5%LiTrifl and it is equal to 421 MPa; in case of PEO/CNT/LiTrifl system it is for PEO/0.1%CNT/5%LiTrifl and it is equal to 170 MPa.

4. Conclusions
LiTrifl salt is effective as electrical resistance reduction at room temperature. Increasing of the LiTrifl content increase electrical conductivity in PEO/CNT/LiTrifl and PEO/GR/LiTrifl system. The highest electrical conductivity in PEO/CNT/LiTrifl system is for PEO/0.25%CNT/25%LiTrifl and it is equal to 81.8·10⁻⁹ S/cm. The highest electrical conductivity in PEO/GR/LiTrifl system is for PEO/0.5%GR/2.5%LiTrifl and it is equal to 1.01·10⁻⁹ S/cm. It is evident that the mechanical properties such as Young’s module are higher for PEO/GR/LiTrifl system. Addition of LiTrifl as plasticizer to PEO/CNT and PEO/GR system decrease crystallinity and thus decrease melting temperature of the samples.

5. References
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