

Short communication

## Physico- and electrochemistry of composite electrolytes based on PEO-DME–LiTFSI with TiO<sub>2</sub>

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### Abstract

The effect of fumed TiO<sub>2</sub> fillers (pure and modified by H<sub>2</sub>SO<sub>4</sub>) on ionic conductivity of composite electrolytes based on poly(ethylene oxide) dimethyl ether (PEODME) oligomer ( $M_w = 500$ ) doped with lithium bis-(trifluoromethanesulfonyl)imide LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> (LiTFSI) are studied by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR) and complex impedance methods. The electrochemical stability of the electrolytes in the potential range of 4 V versus Li electrode has been confirmed by voltammetric measurements. Li electrode reactions have been followed by means of impedance spectroscopy. The growth in time of the resistance of the interfacial (Li electrode–polymer electrolyte) layers was inhibited upon the addition of fillers.

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**Keywords:** Poly(ethylene oxide) dimethyl ether (PEODME); Lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI); Composite polymer electrolyte; TiO<sub>2</sub> pure and modified by H<sub>2</sub>SO<sub>4</sub>; Conductivity; Lithium cell

### 1. Introduction

Polymer electrolytes have been investigated due to the possibility of their application in a variety of electrochemical devices working from subambient to moderate temperature range [1,2]. A lot of work related to ionically conducting polymer matrices present in the literature are devoted to complexes of poly(ethylene oxide) (PEO) or modified PEO with alkali metal salts. The properties of polyether based polymer electrolytes have been modified from the viewpoint of their application. Methods of modification which use inorganic fillers, such as silica, zeolites, titanium or aluminum oxides as additives, offer same advantages compared to the other routes of modifications [1,2]. Addition of inorganic fillers results in improved ionic conductivity, extended thermal stability range, better electrochemical stability and compatibility between electrolyte and electrode as reviewed by Zhou and Fedkiw [3].

Another promising method to enhance the ionic conductivity of crystalline polyether electrolytes is to incorporate lithium salts with a large anion such as lithium bis-

(trifluoromethanesulfonyl)imide (LiTFSI) which are expected to lower the crystallization of PEO–LiTFSI complexes and enhance the conductivity [4,5]. The addition of salts having large anions with dispersed charged also results in reducing fraction of ionic associates which hence leads to an increase in the cation transport number.

The effect of fumed oxide filler (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>) on ionic conductivity of composite electrolytes based on PEO oligomers with LiTFSI has been studied by Zhou and Fedkiw [3]. It was shown that the addition of fillers stiffens polymer segments and no reduction in ion pairing is observed. Our previous studies showed [6] that besides the size of inorganic filler also the type of surface groups has an important effect on ion–ion and ion–polymer interactions. The addition of fillers with Lewis acid surface groups usually leads to the reduction in ion pairing and therefore to an increase in the conductivity. This is due to the interactions of acidic filler centers with anions being considered as Lewis bases. These interactions lead to the release of cations from ion pairs and higher aggregates and therefore to an increase in the cation transport numbers as confirmed by the studies of Scrosati's group [7,8]. However, it has been also noticed that the addition of a strong Lewis acid often leads to the degradation of polymeric chains [9]. Therefore, according to the procedures commonly use in chemical catalysis we decided to soften the

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later effect by the attachment of a strong acid group to the inert filler support.

In the present paper the effect of fumed oxide fillers  $\text{TiO}_2$  pure and modified with  $\text{H}_2\text{SO}_4$  on the ionic conductivity of a composite electrolyte based on PEO/DME with LiTFSI as a dopant are studied by differential scanning calorimeter (DSC), Fourier transform infrared spectroscopy (FT-IR) and complex impedance method. We have used low-molecular weight polyether analogues to obtain single phase amorphous systems at ambient temperatures and limit possible side effects due to the crystallization of the polymer matrix. The electrochemical stability window of the electrolytes in the potential range of 4 V has been confirmed by voltammetric measurements. Li electrode reactions have been followed by means of impedance spectroscopy technique.

## 2. Experimental

### 2.1. Sample preparation

PEODME ( $M_w = 500$ , Aldrich) was filtered and dried on a vacuum line at  $\sim 60^\circ\text{C}$  for 72 h and then, under vacuum of  $10^{-5}$  Torr, stringently freeze-dried using freeze-pump-thaw cycles. While still under vacuum, the polymer was transferred to an argon filled dry-box (moisture content lower than 2 ppm) where the salt was dissolved into the polymer using a magnetic stirrer. The salt content was ranging from 1 to  $5 \text{ mol kg}^{-1}$  of polymer.

$\text{LiN}(\text{CF}_3\text{SO}_2)_2$  (LiTFSI) (Aldrich, reagent grade) was dried under vacuum at  $120^\circ\text{C}$  prior to dissolution. The composite electrolytes were obtained by the dispersion of  $\text{TiO}_2$  in a PEO/DME–LiTFSI solutions. The concentration of  $\text{TiO}_2$  in the composite electrolytes was equal to 10 mass% of the PEO/DME.

Two types of  $\text{TiO}_2$  fillers of different grain sizes were used as additives. Plain  $\text{TiO}_2$  of the size equal to 21 nm and surface modified  $\text{TiO}_2$  (P 25, Degussa) which was used as acid group carrier. The initial grain size of the latter powder was roughly 0.4–0.6  $\mu\text{m}$ . The surface modification was performed by impregnating particles with aqueous solutions of  $\text{H}_2\text{SO}_4$  whose concentrations were calculated to obtain mixtures containing 4 wt% of the acid [10]. (The acidity of the obtained fillers is higher than for  $\text{H}_2\text{SO}_4$  itself and such systems are often named superacids in chemical catalysis.) Then grains were milled in mortar and sieved in order to obtain a homogeneous thin powder (average size of about 10  $\mu\text{m}$ ). Fillers were then dried under vacuum of  $10^{-5}$  Torr at  $150^\circ\text{C}$  for 72 h prior to addition to the polymer–salt mixture. The sulfonated filler preparation procedure differed slightly from those applied in our previous studies [11].

### 2.2. Impedance spectroscopy

Ionic conductivity was determined using the complex impedance method in the temperature range from  $-20$  to  $70^\circ\text{C}$ . The samples were sandwiched between stainless steel blocking electrodes and placed in a temperature controlled oven. Experiments were performed in a constant-volume cylindrical cell with

an electrode diameter of 7.8 mm and fixed electrolyte thickness of 1.6 mm. The cell was placed in a glass vacuum chamber which was evacuated at  $10^{-2}$  Torr for 2 h prior to the experiments. The impedance spectroscopy studies were carried out under static vacuum.

The same conditions were applied at room temperature for the investigations of Li/electrolyte/Li symmetric cells. The impedance spectra were registered over a long time period (150 h). All impedance measurements were carried out on a computer-interfaced Solartron-Schlumberger 1255 impedance analyzer over the frequency range from 1 Hz to 1 MHz. The reproducibility of impedance spectroscopy results was checked by multiple experiments performed at room temperature and analyzed in comparison with typical equivalent circuit proposed in previous studies [12]. The results obtained for samples of the same composition do not differ by more than 10%.

### 2.3. FT-IR

Infrared absorption spectra were recorded on a computer-interfaced Perkin-Elmer 2000 FT-IR system with a wavenumber resolution of  $2 \text{ cm}^{-1}$ . FT-IR studies were performed at  $25^\circ\text{C}$ . Samples were sandwiched between two NaCl plates and placed in the FT-IR temperature-controlled cell; the accuracy of the temperature was estimated to be  $\pm 1^\circ\text{C}$ .

### 2.4. DSC studies

DSC experiments were performed on Perkin-Elmer Pyris 1 scanning calorimeter equipped with a low temperature measuring head and liquid-nitrogen-cooled heating element. Samples in aluminum pans were stabilized by slow cooling to  $-90^\circ\text{C}$  and then heated at  $20^\circ\text{C min}^{-1}$  to  $30^\circ\text{C}$ . An empty aluminum pan was used as a reference. The estimated error of the determination of the glass transition temperature ( $T_g$ ) is  $\pm 2^\circ\text{C}$ .

## 3. Results and discussion

Fig. 1 shows the isotherms of ionic conductivity of PEO/DME–LiTFSI electrolytes without and with 10 mass% of  $\text{TiO}_2$  or  $\text{TiO}_2/\text{H}_2\text{SO}_4$  additives measured at  $-20$ , 20 and  $50^\circ\text{C}$  as a function of salt concentration. Ionic conductivity isotherms measured at 20 and  $50^\circ\text{C}$  do not show any differences between samples; the filler does not have a significant effect on conductivity. The conductivity decreases with increasing lithium salt concentration. The same situation is observed for isotherm measured at  $-20^\circ\text{C}$  for samples containing 3, 4 or  $5 \text{ mol kg}^{-1}$  LiTFSI. For samples with 1 and  $2 \text{ mol kg}^{-1}$  of lithium salts we have observed variation in conductivity depending on sample compositions. For these samples the crystallization process was observed at  $\sim 0$ – $6^\circ\text{C}$  range. Therefore, the drop in the conductivity observed in Fig. 1 can be explained by the presence of crystalline polymeric phases.

Fig. 2 presents ionic conductivity of PEO/DME–( $1 \text{ mol kg}^{-1}$ ) LiTFSI without and with 10 mass% of  $\text{TiO}_2$  or  $\text{TiO}_2/\text{H}_2\text{SO}_4$  measured at low temperature range. At temperatures lower than  $10^\circ\text{C}$  the highest conductivity has been measured for samples

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