



# A novel polymer electrolyte membrane for application in solid state lithium metal battery

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## ABSTRACT

Polyethylene oxide (PEO), dimethyl sulphoxide (DMSO) and lithium trifluoromethanesulfonate ( $\text{LiCF}_3\text{SO}_3$ ) salts are combined into a composite polymer electrolyte studied for application in lithium metal battery. FTIR measurements and AFM images are used to reveal the structure and morphology of the polymer electrolyte, while electrochemical impedance spectroscopy (EIS), chronoamperometry and voltammetry are employed for determining the electrolyte conductivity, lithium transference number, chemical and electrochemical stability, respectively. The data reveal a suitable conductivity and lithium transport, i.e.,  $\delta$  above  $10^{-4} \text{ S cm}^{-1}$  and  $t_{\text{Li}^+}$  about 0.5, at moderate temperature, which allow the use of the membrane and a  $\text{LiFePO}_4$  olivine cathode in an efficient lithium metal cell delivering a capacity of  $130 \text{ mAh g}^{-1}$  at about 3.4 V, and operating at  $50^\circ\text{C}$ . This relatively low operating temperature, the good electrochemical properties, and the polymer configuration of the PEO-DMSO- $\text{LiCF}_3\text{SO}_3$  membrane suggest it as a viable solution for application in high energy lithium metal battery.

## 1. Introduction

Polymer electrolytes have been extensively investigated as promising candidates for solid state lithium battery due to their mechanical flexibility, and scalability to the *thin-film* conducting configuration [1]. Among these very interesting materials, polyethylene oxide (PEO) has attracted particular attention due to its suitability for dissolving various salts in a vast range of concentrations, in combination with nanometric ceramics [2] which allow relevant mechanical stability and enhance the ionic conductivity [3]. However, the suitability of PEO-based membranes at temperatures exceeding  $65^\circ\text{C}$  to allow amorphous state and proper ion conduction still hinders its large scale diffusion [4]. Indeed, PEO chains have an extended helical structure with repeating units in turns of the helix. The ether oxygen of the chains coordinates the cations and forms stable polymer-ion complexes, while the anions are dispersed within the polymer matrix [5]. Besides, the chains form thin crystalline plates which, in turn, are arranged in thin stacks, and finally into spherical crystals separated by an amorphous polymer phase. Generally, this *semi-crystallinity* covers about 60% of the PEO bulk at room temperature, while the amorphous elastomeric phase, which strongly favors the segmental motion and the efficient ion transport

through polymer of the PEO-salt complexes, constitutes the remaining part [6]. The presence of extended crystalline regions within PEO-based electrolytes at the room temperature strongly limits the long-range diffusion of the ions, and lowers the ionic conductivity [7]. The ion transport and conductivity may be actually enhanced by increasing the ratio of the amorphous elastomeric state with respect to the crystalline one in the electrolyte adopting various approaches, including the abovementioned nanometric ceramic addition, to obtain the nanocomposite polymer electrolytes (NCPes) [8], the use of Ionic Liquids (ILs) [9,10] as well as the employment of various solvents as plasticizer agents [11]. A very interesting approach consisted of the use of emulsifying agents such as DMSO, which forms thermodynamically stable DMSO/Li ion molecules [12,13]. However, the very poor SEI forming ability of DMSO-lithium salt emulsions strongly limited their use as the electrolyte media in lithium cells [14]. Following this trend, we advantageously combined the mechanical and electrochemical stability features of the PEO, and the highly ion-conducting nature of the DMSO, in a new electrolyte studied for application in polymeric lithium metal battery. The electrolyte is fully characterized in terms of conductivity, ion transport characteristics, chemical and electrochemical stability, and employed in an efficient lithium metal battery using  $\text{LiFePO}_4$

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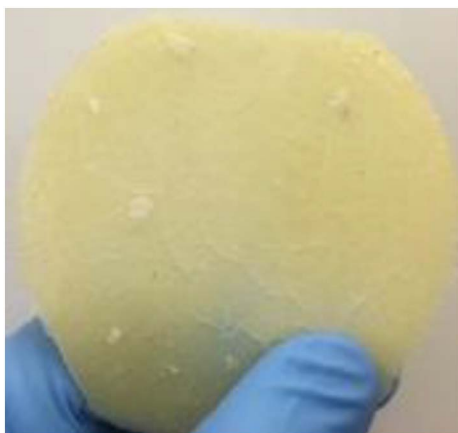


Fig. 1. Photographic image of the PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>DMSO solid polymer electrolyte membrane. See Experimental section for sample identification.

electrode [15].

## 2. Experimental

Linear PEO with a molecular weight of 600,000 g mol<sup>-1</sup> (Sigma Aldrich) and DMSO (Sigma Aldrich) in a proportion of 1.7 g of PEO to 1.5 ml of DMSO, and 0.3 g of LiCF<sub>3</sub>SO<sub>3</sub> (Sigma Aldrich, battery grade), were dissolved in acetonitrile (Sigma Aldrich, battery grade), stirred for 2 h at a temperature of 60 °C, transferred to glass petri dish and kept at 80 °C overnight in an oven. The molar ratio of the Li in salt to oxygen in EO was 1:20, therefore the membrane is indicated in the work by PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>DMSO. The membrane was subsequently dried at 50 °C for 5 days under vacuum, in order to remove traces of water or solvent, and transferred to a glove box (M brown) with water and oxygen content lower than 1 ppm. The final membrane (photographic image in Fig. 1) with a thickness of about 350 μm was characterized by good mechanical stability. A control sample with the same composition, indicated by PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub> was prepared following similar procedure without DMSO for comparison.

FTIR spectra of PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>DMSO and PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub> were performed using an ATR-FTIR Perkin Elmer Spectrum 100 series, scanning in the range of 600–4000 cm<sup>-1</sup>. Atomic force microscopy images were collected using a AFM JEOL JSM-7600F instrument. Conductivity measurements were performed on 2032 coin-cell with Teflon O-ring having internal diameter of 10 mm and thickness of 320 μm to determine the cell constant, using a frequency analyzer Princeton Advanced Research (VersaSTAT3F) in 0.5 MHz–0.1 Hz frequency range with signal amplitude of 10 mV. The conductivity data were collected every 5°, and every 2° near by the transition temperature during cooling and subsequent heating. Before cooling measurement, the cell was held at 80 °C for at least 12 hours. Galvanostatic cycling was performed using a Maccor series 4000 battery test system on Li/PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>DMSO/LiFePO<sub>4</sub> 2032 coin-cell in the potential range of 3.0–4.0 V at current rate of C/10 (1C was 0.665 mA cm<sup>-2</sup>, as calculated with respect to the electrode geometric surface considering the LiFePO<sub>4</sub> active mass, i.e., 4 mg cm<sup>-2</sup>, and its theoretical capacity, i.e., 170 mAh g<sup>-1</sup>) [15], at temperatures of 50 °C. The Li/PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>DMSO interface stability was measured at 50 °C by impedance spectroscopy using a VersaSTAT3F instrument on symmetrical lithium/lithium 2032 coin-cell in 0.5 MHz – 0.1 Hz frequency range and signal amplitude of 10 mV. Electrochemical stability window was determined by linear sweep voltammetry on three electrode cell using the PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>DMSO membrane as the electrolyte, Li as the counter and reference electrode, and Super P on Al as the working electrode, with a scan rate of 0.1 mV s<sup>-1</sup> and voltage ranging between the OCV and 4.5 V, employing a VersaSTAT3F instrument. The lithium

transference number was measured with the same instrument at 50 °C by adopting the Bruce Vincent method which involved current monitoring during time upon the application of a 30 mV direct-current (DC) signal to a symmetrical Li/PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>DMSO/Li cell until the steady state was reached, and impedance measurement immediately before, and after DC-current application [16].

## 3. Result and discussion

Intermolecular interactions, and plasticizing effect of DMSO on PEO are investigated by FTIR measurements carried on the PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>DMSO polymer electrolytes and reported in Fig. 2. The figure shows a band at 844 cm<sup>-1</sup> (tagged by 1 in Fig. 2A and magnified in the top-left panel of Fig. 2B) assigned to the antisymmetric rocking mode of CH<sub>2</sub>-CH<sub>2</sub> coupled with the COC symmetric stretching mode, a band at 963 cm<sup>-1</sup> (tagged by 2 in Fig. 2A and magnified in the top-right panel of Fig. 2B) primarily associated with the CH<sub>2</sub> antisymmetric rocking mode with appreciable contribution of the COC antisymmetric stretching mode [17], a band at 1102 cm<sup>-1</sup> (tagged by 3 in Fig. 2A and magnified in the bottom-left panel of Fig. 2B) mainly associated with the COC antisymmetric stretching mode, and a band at 1345 cm<sup>-1</sup> (tagged by 4 in Fig. 2A and magnified in the bottom-right panel of Fig. 2B) due to the hybridized mode of the CH<sub>2</sub> antisymmetric wagging and twisting modes of the CH<sub>2</sub>-CH<sub>2</sub> group of PEO. The lower wave-number region provides information about the modifications in local structure of host polymer due to the interaction of DMSO with polymer backbone. The intensity decrease of the two characteristic bands at 844 cm<sup>-1</sup> and 963 cm<sup>-1</sup> in the composite electrolyte evidences a distortion of the helical configuration of PEO polymer backbone, due to the plasticizing effect of DMSO [18,19]. In addition, the shift of the bands at 1102 and 963 cm<sup>-1</sup> reveals a decrease of the O-C-C-O torsional angle in the electrolyte with respect to pure PEO, as already demonstrated by ab initio calculations reported in literature [20], thus further suggesting the DMSO plasticizing effect on the PEO polymer matrix. The peak at 1042 cm<sup>-1</sup> in the case of DMSO (tagged by 5 in Fig. 2A) is due to S-O vibrational stretching, which is shifted to 1030 cm<sup>-1</sup> in PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>DMSO, thus indicating the association of DMSO with PEO and/or Li ion. In addition, the peaks between 3000 cm<sup>-1</sup> to 2700 cm<sup>-1</sup> (tagged by 6 in Fig. 2A) are assigned to the C-H stretching of the PEO backbone and the methyl of DMSO. The peak at 1466 cm<sup>-1</sup> (tagged by 7) is assigned to the C-H deformation of the PEO backbone. In the spectrum of DMSO the peaks at 1436 and 1404 cm<sup>-1</sup> (tagged by 8) are assigned to the antisymmetric bending of CH<sub>3</sub>, while the peak at 1306 cm<sup>-1</sup> (tagged by 9) is assigned to symmetric deformation of CH<sub>3</sub> group that are attached to the sulfur atom.

The plasticizing effect of DMSO on PEO matrix was further investigated by using an atomic force microscope (AFM). Fig. 3 shows the three dimensional topography images of PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>DMSO membrane (A) and PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub> blank (B). The images reveal smoother surface of PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>DMSO (Fig. 3A) compared to PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub> (Fig. 3B), which is most likely due to the decrease of membrane tortuosity caused by the addition of the DMSO plasticizer. Indeed, the latter increases the ratio of the amorphous phase of the PEO matrix with respect to the crystalline one, thus facilitating the segmental rearrangement of polymer chain and, therefore, the ion movement [21].

Fig. 4 shows the Arrhenius conductivity plots of the PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>DMSO electrolyte membrane during cooling from a temperature of about 80 °C to 40 °C (A) and heating back to about 80 °C (B), as well as the steady state conductivities in a similar temperature interval of the PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub> blank (indicated by stars in each panel). During cooling (Fig. 4A) the Arrhenius plot of the PEO<sub>20</sub>LiCF<sub>3</sub>SO<sub>3</sub>DMSO electrolyte exhibits the typical trend of the PEO-based polymer membranes, with slope change around 50 °C corresponding to the conductivity decrease during the transition from amorphous to crystalline phase (generally to spherical crystalline stacks). Furthermore, the electrolyte reveals a higher conductivity with respect to the blank

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