

Electrochemical and Thermal Properties of PEO-LITFSI based Gel Polymer Electrolytes with the Effect of Plasticizer and Filler for Lithium-sulfur Batteries

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Abstract: Electrochemical properties and interfacial stability of poly (ethylene oxide) (PEO) / lithium (bis) trifluoro-methane-sulfonate imide (LITFSI) with the incorporation of plasticizers (TEGDME & DIOX) and filler (SiO₂) based composite gel polymer electrolytes prepared by the simple solution casting technique has been studied. The addition of plasticizers and filler with polymer electrolytes enhances the ionic conductivity at low temperature. The interfacial stability, transport properties and thermal stability were remarkably improved by the addition of SiO₂ and plasticizers into the polymer-salt complex matrix. The sample with 2% of plasticizers was found to be optimal in ionic conductivity point of view.

Keywords: PEO, Composite gel polymer electrolyte, Ceramic filler, interfacial stability, transport properties

1. INTRODUCTION

A battery based on Lithium metal/elemental sulfur redox couple has a theoretical capacity of 1672 mAhg⁻¹ and specific energy of 2600 Wh/kg, assuming the complete reaction of Li with sulfur to Li₂S. The use of elemental Sulfur as cathode material for Li batteries is useful because it is relatively cheap and low toxic material [1]. It has been reported that Li-S cells with liquid electrolytes have serious problems of utilization with low active and poor life-cycle [2-6]. The above problems may be arising due to the insulating nature of sulfur and the formation of polysulfides during the discharge process. The first step is the formation of sulfur into LiS_n and it is dissolved into electrolytes. The second step is change of LiS_n to Li₂S. This process of dissolution causes an irreversible loss of active material. To overcome this problem polymer electrolytes such as PEO- Li salt complex can be introduced to reduce the dissolution of polysulfide into the electrolyte. However, these PEO-salt complexes have some problems like reactivity of the lithium anode at higher temperature and low ionic conductivity at low temperature. To resolve these problems plasticizers and ceramic filler such as Al₂O₃, SiO₂ and TiO₂ are added to PEO based polymer electrolytes [7-9]. It has been reported that an additive

improved conductivity, decrease in value of interfacial resistance which increases the amorphous nature of PEO. Plasticizers like TEGDME and DIOX act as solvents for lithium salt and effectively reduce the viscosity of the electrolyte medium [5, 10].

In the present work, PEO with Li (CF₃SO₂)₂N salt, the combination of plasticizers such as TEGDME, DIOX and SiO₂ as filler was used as starting materials to prepare polymer electrolyte for Li-S battery, because of its favorable interfacial stability and electrochemical properties. The low molecular weight and higher value of dielectric constant based plasticizer was used to enhance the conductivity of polymer electrolytes. Various research reports have offered to enhance the conductivity at lower temperature. The addition of ceramic filler (SiO₂) is effective to enhance the conductivity at lower temperatures as well as its mechanical properties. The prepared electrolyte films have been subjected to Electrochemical Impedance spectroscopic analyzer, thermogravimetry/differential thermal analysis (TG/DTA), interfacial stability and the transport properties.

2. EXPERIMENTAL

PEO with average molecular weight 3×10⁵ (procured from Sigma Aldrich, USA) and lithium (bis) trifluoro methanesulfonate imide, LiTFSI (procured from E-Merck, Germany) were dried in vacuum for 48 hours at 50 °C and 100°C, respectively. Prior to use,

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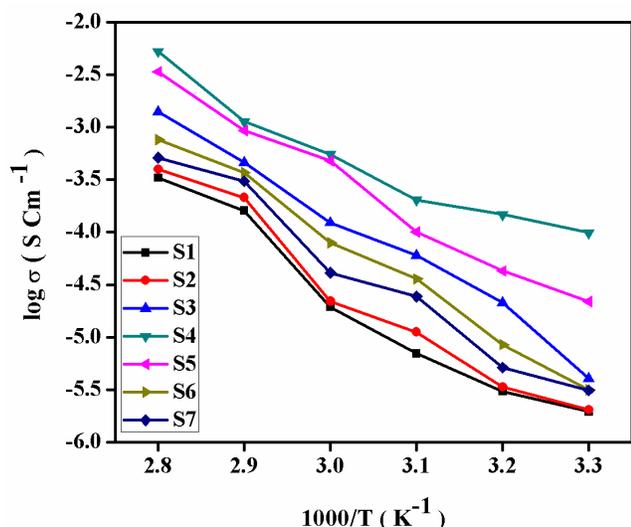


Figure 1. Variation of ionic conductivity as a function of inverse temperature ($1000/T$) for various concentrations of filler and plasticizers.

tetra ethylene glycol dimethyl ether (TEGDME) and 1, 3-dioxolane (Grand Core, battery grade from Sigma Aldrich, USA) was dried over 4\AA molecular sieves for the time period of 48 hours. Before use, the filler SiO_2 was dried in vacuum at 90°C for 96 hours. The solvents TEGDME and DIOX maintained in the ratio of 1:1 was used as the plasticizer as well, this combination is found to be optimum for Li-S batteries [11]. All the samples were prepared by solution casting technique in an argon atmosphere [12, 13]. The appropriate weights of PEO, $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ salt, plasticizers and filler were dissolved in anhydrous acetonitrile and stirred continuously until the mixture formed a homogeneous viscous liquid. The resulting solution was transferred into a Teflon disc and the acetonitrile was allowed to evaporate completely at room temperature. The free standing films with flexible standing nature around 100 microns were obtained and the prepared samples were dried for 12 hours at a temperature around 50°C to mark out the traces of acetonitrile.

The ionic conductivity of the prepared samples was analyzed with the help of Stainless Steel plates as blocking electrodes using Electrochemical Impedance spectroscopic analyzer (Zahner IM6 (Germany)) within the temperature range between 303-353 K. Thermogravimetric analysis of the prepared samples was done using TG/DTA analyzer (TA instrument, USA) under inert atmosphere with in the scan rate of 10°C per minute. The compatibility studies were performed by non-blocking symmetric cells and were investigated studying time dependence impedance analysis technique at 30°C . The transference number of Li was calculated using the method given by Vincent and his co-workers according to the following Equation (1) [14, 15, 16].

$$Li_t^+ = \frac{I_{ss}(V - I_0 R_0)}{I_0(V - I_{ss} R_{ss})} \quad (1)$$

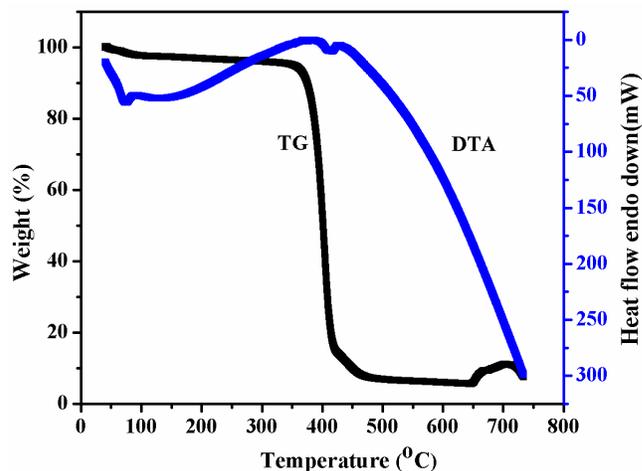


Figure 2. TG/DTA traces of sample S_4 .

3. RESULTS AND DISCUSSION

3.1. Conductivity Measurement

The electrochemical impedance spectroscopic analysis has been used to characterize ionic conductivity and interfacial stability of materials. The lower value ionic conductivity in a polymer complex results from the crystalline phase which affects the mobility of the ions. The ionic conductivity of PEO-based gels with Li salt and SiO_2 as filler has been analyzed as a function of temperature which is shown in Figure 1. It has been found that as temperature increases, the value of conductivity increases for all the compositions which may be due to increase in value of plasticizer content and PEO. It is also observed that a sudden increase in value of conductivity at approximately 65°C for the entire polymer electrolyte films which are the usual characteristics of most PEO-based polymer electrolytes. This is associated with the increase in the amorphous nature of PEO. The sample S_4 showed high ionic conductivity and the ionic conductivity of the samples were reduced with further increase of plasticizers and is attributed to the higher viscosity of the membrane [17-19]. Therefore, a low filler and plasticizer content would contribute to the dissociation of the lithium salt, resulting in an enhancement of the total ionic conductivity. But, at high contents of both the continuous non-conductive phase built up by the large amount of fillers and plasticizers as an electrically inert component would block lithium ion transport, resulting in an increase in the total resistance of the composite gel polymer electrolyte. It should be noted that membrane beyond 2% of plasticizers was not freestanding. Therefore, for all further characterizations samples (S_4) were used.

3.2. TG DTA Analysis

In order to examine the thermal stability of the polymer electrolyte with maximum conductivity, the film was subjected to TG/DTA analysis in the range 0°C to 700°C at a heating rate of $10^\circ\text{C}/\text{min}$. The TG/DTA spectrum of the polymer electrolyte sample with high conductivity is shown in figure 2. The TG curve shows a first degradation at 90°C accompanied by a weight loss of 7%, which may be due to the evaporation of water molecule absorbed by the sample during loading or the volatile impurities pre-

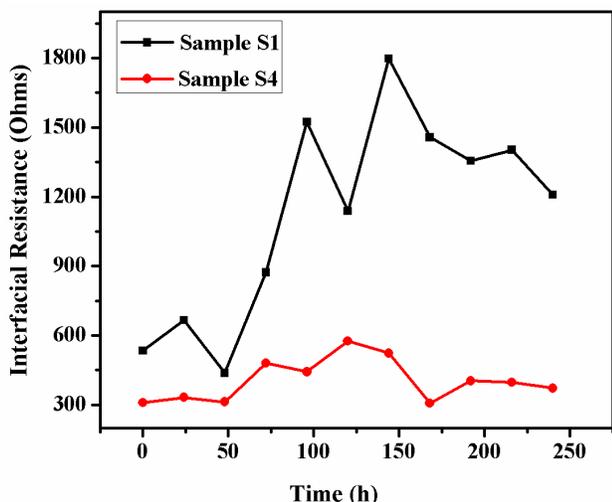


Figure 3. Variation of interfacial resistance (R_i) as a function of time for the symmetric cells comprising Li/CGPE/Li cells at 30 °C.

sent [20,21]. The film is found stable up to 332°C and beyond 332°C the film loses its weight drastically up to 470°C. This could be attributed to the decomposition of the polymer electrolyte. The exothermic peaks observed around 79 °C and 682 °C indicate the transition of the composite polymer electrolyte accompanied by a weight loss. The remaining residue around 50% may be due to the presence of plasticizers and SiO₂. It is concluded that the addition of inorganic filler effectively increased the thermal stability of the electrolyte. These results indicate that the samples are stable up to 332°C.

3.3. Interfacial Properties

In the present study, in order to ascertain the interfacial stability of CGPE with lithium metal electrodes the symmetric cell composed of Li/CGPE/Li was assembled and its interfacial resistance values were measured as a function of time. Figure 3 illustrates the variation of interfacial resistance, R_i as a function of time for the sample S₁ and for sample S₄ at 30 °C. The values of interfacial resistance can be measured from the Cole-Cole impedance plots in which the large semicircles represent a parallel combination of resistance (R_{film}) and capacitance associated with the passivation film on the lithium metal anode [22].

The interfacial resistance value of the sample S₁ (without plasticizers and filler) increases and decreases in an irregular manner. However, the values of the interfacial resistance of plasticizer and SiO₂-added samples are substantially lower than that of the filler-plasticizer free sample. As is clearly evident, for the sample S₄ the resistance values remain more or less the same even after 264 hours. This is attributed to the morphological changes of passivated film with time, which, of the composite polymer electrolytes has been significantly reduced upon the incorporation of the SiO₂ (much lower than S₁ sample).

3.4. Lithium Transference Number

The transference number of Lithium ion is an essential factor

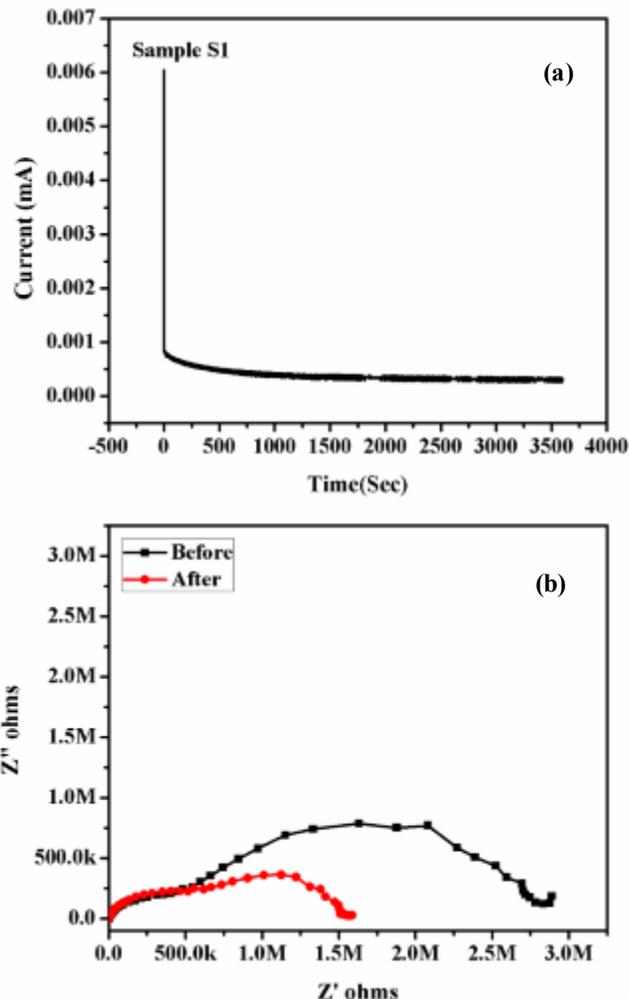


Figure 4. Chronoamperometric curve of Li/CGPE/Li cell after a perturbation of 10 mV dc pulse. (a) Cell with sample S₁ and (b) Impedance spectrum of the cell before and after the dc polarization at 30 °C, respectively.

which guarantees the performance and capability rate of lithium ion batteries for high power applications such as hybrid electric vehicles [23]. The transference number of Li ion is calculated using Eq.(1) [14]. The value of a lithium transference number of samples (S₄) with the incorporation SiO₂ has been calculated and the value is 0.8 which is sufficient for battery applications. The value of conductivity increases, whereas the value of transport number increases, which indicates that the addition of filler with the combination of plasticizers facilitate the combination of ion pairs and charge separation due to addition SiO₂ as a filler [24]. Figure 4 (a and b) shows the chronoamperometric curves (without plasticizer and filler) and Nyquist plot for sample S₁ before and after perturbation for sample S₁ respectively. Similarly Figure 5 (a and b) for sample S₄ (with plasticizer and filler). It is obvious that there is a slight difference between initial and final resistances R_0 and (R_{ss}) of two intervals of Li, which confirms the stability of the lithium metal electrode with SiO₂ and plasticizers incorporated CGPE. The

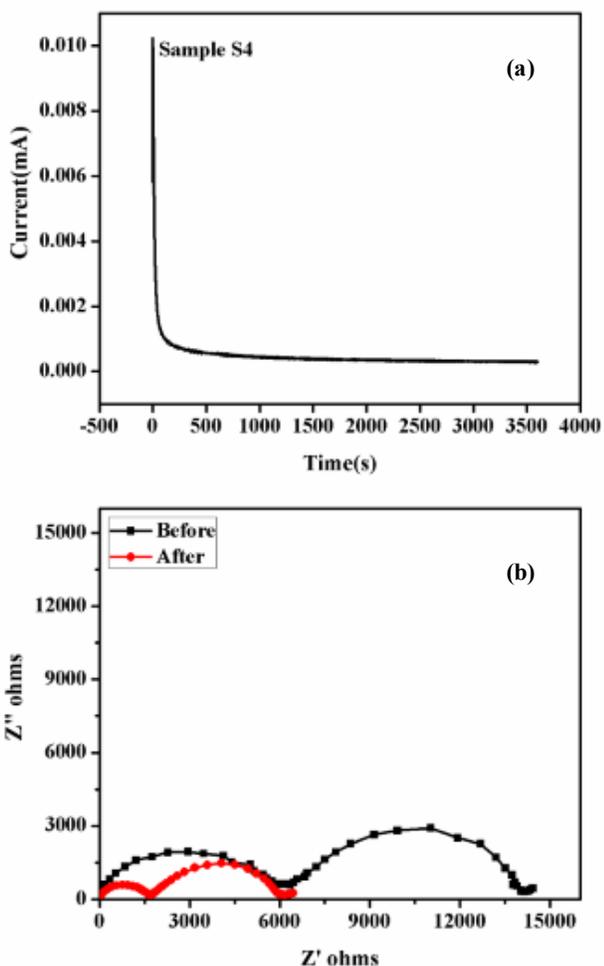


Figure 5. Chronoamperometric curve of Li/CGPE/Li cell after a perturbation of 10 mV dc pulse. (a) Cell with sample S₄ and (b) Impedance spectrum of the cell before and after the dc polarization at 30 °C, respectively.

semicircles are observed at higher and middle frequency regions indicating the value of transfer resistance (R_{ct}) and Faradaic redox process involved in the exchange of Li^+ ions [25].

4. CONCLUSIONS

PEO-based composite gel polymer electrolytes with different compositions of PEO, SiO_2 combination of plasticizers and LITFSI were prepared using simple solution casting technique. The ionic conductivity of the prepared gel polymer electrolyte increases with the increase of concentration of plasticizer and PEO. TG/DTA analysis showed that the thermal stability of the prepared polymer electrolytes is suitable for the application of Li batteries even at higher temperature. The value of interfacial resistance was found to be lower for plasticizers and filler added samples under open circuit conditions at temperature 30 °C. The transference number of Li was increased by the incorporation of plasticizers and filler to the polymer matrix. As a result, CGPE composed of PEO+ SiO_2 +LITFSI with 2% of plasticizers was found to be suitable for battery applications.

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