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Preparation and characterization of PEO-based composite gel-polymer electrolytes complexed with lithium trifluoro methane sulfonate

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Chitosan has been successfully incorporated as a filler in a polyethylene oxide (PEO) and lithium trifluoromethanesulfonate ($LiCF_3SO_3$) matrix with a combination of plasticizers, namely 1,3-dioxolane (DIOX) and tetraethylene glycol dimethylether (TEGDME). The composite gel-polymer electrolyte (CGPE) membranes were prepared by solution casting technique in an argon atmosphere. The prepared membranes were subjected to SEM, TG/DTA and FT-IR analyses. A Li/CGPE/Li symmetric cell was assembled and the variation of interfacial resistance was measured as a function of time. The lithium transference number (Li_t^+) was measured and the value was calculated as 0.6 which is sufficient for battery applications. The electrochemical stability window of the sample was studied by linear sweep voltammetry and the polymer electrolyte was found to be stable up to 5.2 V.

Keywords: *polyethylene oxide; ionic conductivity; FT-IR; transport number; interfacial properties*

1. Introduction

In recent years, rechargeable lithium-sulfur batteries in which we use sulfur as the cathode and lithium as anode have been the subject of intense research due to their high theoretical specific capacity of 1672 mAh/g and energy density of 2600 W·h/kg [1–3]. The theoretical capacity of Li-S batteries is approximately five times higher than that of conventional Li-ion batteries with transition metal oxide cathodes such as $LiCoO_2$, $LiMnO_2$ and $LiFePO_4$ [4–15]. Also, elemental sulfur has some features such as non toxicity and low cost. Therefore, we can use sulfur as a cathode material rather than transition metal oxides. Here, we concentrate on the preparation of polymer electrolytes to enhance significant applications in power sources, like lithium secondary batteries. In order to improve the electrochemical properties, various approaches have been made to structure polymer electrolytes. Some approaches consist in synthesizing new polymers, cross linking two polymers, blending two polymers, adding plasticizers to polymer electrolytes and inorganic inert fillers to make composite polymer electrolytes [16]. Among these approaches, addition of plasticizers and fillers is a useful technique to enhance the conductivity of polymer systems, using low molecular weight and high dielectric constant additives.

In the present work, we have studied a PEO-based composite gel-polymer electrolyte to improve the room temperature ionic conductivity, thermal stability and interfacial properties of the polymer electrolyte. It has been achieved by the addition of a chitosan nanofiller and plasticizers, namely DIOX and TEGDME, a PEO polymer and a salt matrix. As-prepared composite gel-polymer electrolyte films have been characterized through ionic conductivity, thermal studies, compatibility, transference numbers, surface morphological features and FT-IR analyses.

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2. Experimental

2.1. Electrolyte preparation

PEO (MW = 3 × 10^5, Aldrich, USA) and lithium trifluoromethanesulfonate, LiTf (E. Merck, Germany), were dried under a vacuum for 48 h at 50 °C and 100 °C, respectively. Both tetraethylene glycol dimethyl ether (TEGDME) and 1,3-dioxolane (Grand Cor., battery grade: Sigma Aldrich), were dried in an argon atmosphere with molecular sieves (4 Å) for a 48 h before use. The chitosan filler was also dried under vacuum at 90 °C for 96 h before use. In the present work, a combination of plasticizers, TEGDME/DIOX of 1:1 wt.% was employed. This combination was found to be optimal for Li-S batteries by Zhang et al. [14] when the authors studied the influence of gel electrolytes for confining polysulfides.

The composite gel polymer electrolytes (CGPE) samples were prepared in an argon atmosphere by the solution-casting technique [17, 18]. The appropriate weights of the PEO, $LiCF_3SO_3$, plasticizers and filler were dissolved in an anhydrous acetonitrile and stirred continuously until the mixture took on a homogeneous viscous liquid appearance. We set the total weights of the polymer, DIOX/TEGDME, chitosan and lithium salt to be identical (100 %) for preparing the films of various plasticizer contents and polymer ratios. The mixture was then immediately cast on to a Teflon sheet container and the acetonitrile was allowed to evaporate completely at room temperature. After the evaporation of acetonitrile, mechanically stable, free-standing and flexible films of uniform thickness (100 μm) were obtained. The electrolytes were prepared with different compositions as presented in Table 1. All the electrolytes were prepared in an argon filled glove box (M Braun, Germany) with less than 0.1 ppm of moisture content.

The prepared electrolytes were subjected to an AC impedance analysis, in order to calculate the ionic conductivity. This study was carried out with the help of stainless steel blocking electrodes in the temperatures range of 303 K to 363 K. The ionic conductivity was calculated as $\sigma = t/(R_bA)$, where R_b is the bulk resistance, t is the thickness of the film and A is the area of the film. Among the samples studied, sample S_4 was found to be optimal for battery applications in terms of ionic conductivity. Therefore, in the present work, sample S_4 was used for thermal and spectroscopic characterization. The TG/DTA analysis was performed by using a PerkinElmer diamond TG/DTA analyzer under a N_2 atmosphere with a ramp of 10 °C/min. The surface morphology of the samples was examined by using a scanning electron microscope TESCAN-VEGA3 LMU (SEM) model. FT-IR spectra were recorded in the range of 4000 cm^{-1} to 400 cm^{-1} using a Jasco FT-IR spectrophotometer by the ATR method to identify the complexation behavior of the prepared polymer electrolyte samples. Symmetric non-blocking cells of Li/CGPE/Li were assembled for compatibility studies and were investigated by studying the time dependence of impedance of the systems under open circuit conditions at 30 °C. The lithium transference number was calculated by using equation 1 as proposed in [19–21]:

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

The Li/CGPE/Li cell was polarized by a DC pulse of 10 mV. Time evolution of the resulting current flow was then followed. The initial (I_0) and steady state (I_{ss}) values of the current flowing through the cell during the polarization were measured. The R_0 and R_{ss}, which respectively represent the resistance values before and after perturbation, were obtained from impedance data.

3. Result and discussion

3.1. Conductivity measurements

Fig. 1 illustrates the variation of ionic conductivity as a function of inverse temperature for various concentrations of plasticizer and PEO. The bulk resistance was measured from the high frequency intercept on the real axis. The conductivity of the polymer electrolyte film was calculated from the measured resistance R_b, area A and

Table 1. Composition of polymer, filler, plasticizers and lithium salts.

Sample	Polymer [wt.%]	Nanofillers (*) [wt.%]	$LiCF_3SO_3$ [wt.%]	Plasticizers [wt.%]
S1	90	0	10	0
S2	90	5	5	0
S3	84	5	10	1
S4	83	5	10	2
S5	82	5	10	3
S6	81	5	10	4
S7	80	5	10	5

Polymer: PEO; (*): Chitosan; Plasticizers: (TEGDME + DIOX).

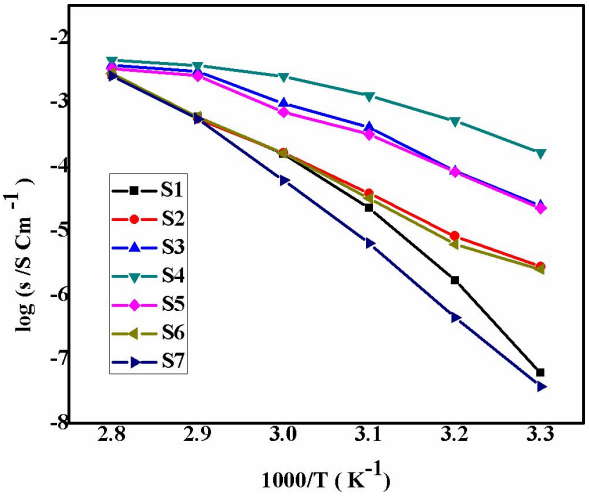


Fig. 1. Variation of ionic conductivity as a function of inverse temperature (1000/T) for various concentrations of filler and plasticizers.

thickness t of the polymer film. It was found that the plasticizers and filler-added electrolytes exhibited a significantly higher conductivity than pure PEO-based samples. Fig. 1 presents the variation of ionic conductivity as a function of the PEO weight ratio in the $LiCF_3SO_3$ complex. In this figure, we can see that the conductivity of the samples increases with the increase of plasticizers and filler content up to a certain level; afterwards, it decreases. The maximum ionic conductivity was observed for the sample S_4 and it was reduced with further increase of PEO /plasticizer concentrations (samples S_5 to S_7) which was attributed to higher viscosity of the membrane. Therefore, a low filler and plasticizers content, would contribute to the dissociation of lithium salt, resulting in an enhancement of the total ionic conductivity. However, at high contents of both, the continuous non-conductive phase built up by the large amount of the fillers and plasticizers as an electrically inert component would block up lithium ion transport, resulting in an increase in the total resistance of the composite gel-polymer electrolyte [22]. It should be noted that a membrane containing more than 2 % of plasticizers was not free-standing [23–25]. Among the samples studied, S_4 was found to be optimal in tuning ionic conductivity. It was, therefore, used for further characterization.

3.2. FT-IR analysis

The FT-IR plots of pure PEO, $LiCF_3SO_3$, DIOX, TEGDME, chitosan and polymer electrolyte complexes are shown in Fig. 2. In pure PEO (Fig. 2a) the bands that appear at 2888 cm^{-1}, 2740 cm^{-1}, 1260 cm^{-1}, 1240 cm^{-1} and 1155 cm^{-1} correspond to symmetrical CH_2-stretching, asymmetrical CH_2-stretching, asymmetrical CH_2-twisting, symmetrical CH_2-twisting and C–O–C asymmetric stretching mode respectively. The region for PEO between 1400 cm^{-1} and: 1050 cm^{-1}, where C–O–C vibrations appear plays a significant role [26]. The band which appears at 3442 cm^{-1} is attributed to the presence of moisture which is due to the hydrophilic nature of PEO [27]. This moisture content could be due to the moisture absorption at the time of loading the sample.

The peak appearing at 3442 cm^{-1} (for pure PEO) is shifted to 3492 cm^{-1} because of the formation of a complex between lithium salt and polymer host. The C–H stretching frequency of PEO appearing at 2883 cm^{-1} is shifted to 2935 cm^{-1} in the complex [28]. The asymmetric bending vibration at 1471 cm^{-1} of pure PEO is shifted to 1467 cm^{-1} and the intensity of the peak is increased and broadened in the polymer complex.

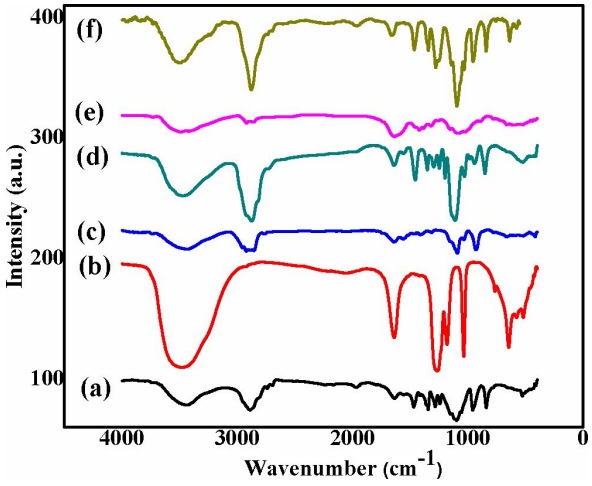


Fig. 2. FT-IR spectra of (a) PEO, (b) LITFSI, (c) DIOX, (d) TEGDME, (e) chitosan and (f) S_4 sample.

The band at 1467 cm^{-1} is attributed to the CH_2 bending vibration in the complex. Moreover, the peaks found at 1341 cm^{-1} and 1337 cm^{-1} are assigned to CH_2 wagging. The peaks at 1152 cm^{-1}, 1059 cm^{-1}, 961 cm^{-1} and 839 cm^{-1} for pure PEO appear in the same range as in the polymer complex. The peaks which appear at 1282 cm^{-1} and 1241 cm^{-1} disappear after the complex formation. The peaks which appear for pure salt at 3484 cm^{-1} and 1642 cm^{-1} reduce their intensity in the complex. Similarly, the peaks at 1033 cm^{-1} and 642 cm^{-1} disappear after the complex formation [29]. The shifting of the peaks, the disappearances of existing peaks and the formation of new peaks in the electrolyte systems indicate polymer-salt interaction in the plasticizer and filler-incorporated composite gel-polymer electrolytes.

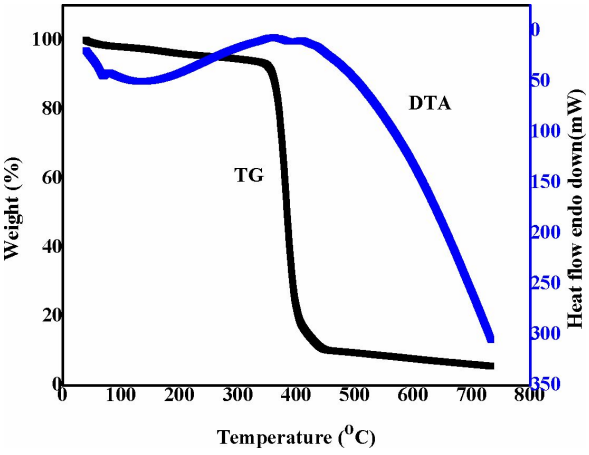


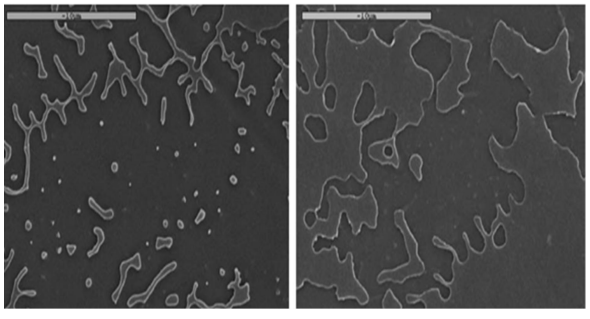
Fig. 3. TG/DTA traces of S_4 sample.

3.3. TG-DTA analysis

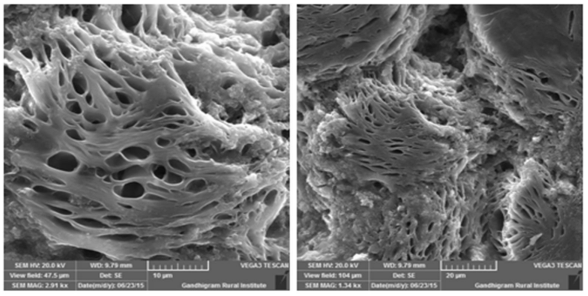
In order to examine the thermal stability of the polymer electrolyte, sample S_4 was subjected to a TG/DTA analysis between 0 °C and 700 °C at a heating rate of 10 °C·min^{-1} (Fig. 3). From the themogram, it is observed that sample S_4 is thermally stable up to 362 °C. The TG curve shows a first degradation at 90 °C accompanied by a weight loss of approximately 2 %, which may be caused by the evaporation of the water molecules absorbed by the sample at the time of loading and also due to the volatile impurities present in it [30, 31]. Further, the irreversible decomposition takes place at 362 °C which indicates that the CGPE is thermally stable up to 362 °C which is fairly higher than the operating temperature of Li-S batteries. It can be concluded that the addition of chitosan has effectively increased the thermal stability of the electrolyte.

3.4. Scanning electron microscope (SEM) analysis

Sample S_1 and sample S_4 (having the maximum ionic conductivity) were subjected to a scanning electron microscopic analysis and their surface images are shown in Fig. 4a and Fig. 4b, respectively. In Fig. 4a, the image shows islands and this morphology does not encourage conduction. According to Chu et al. [32], the morphology of polymeric membranes can be tailored or modified by the incorporation of lithium salt and filler in



(a)



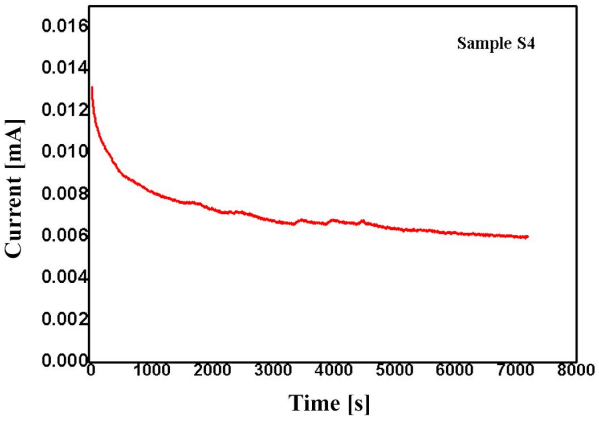
(b)

Fig. 4. SEM images of samples (a) S_1 and (b) S_4.

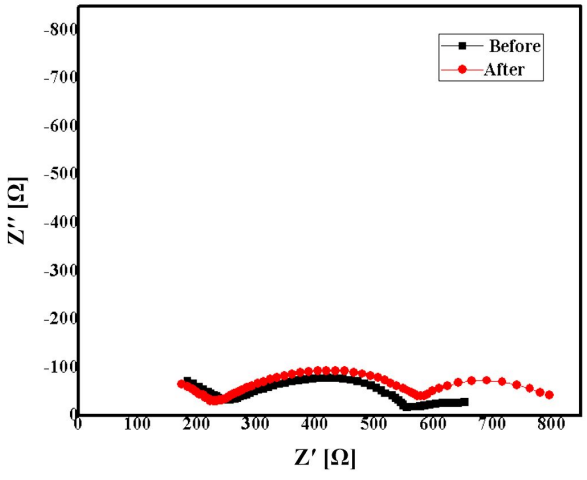
the polymer electrolyte system. In the image of S_4, it is observed that the presence of the high number of pores is responsible for high ionic conductivity. These pores are caused by the addition of plasticizers and fillers; they also help to absorb the large volumes of liquid accounting for the increased conductivity [33]. The presence of pores in the microstructure is mainly due to the solvent removal [34, 35] and by solvent retention ability of the electrolyte system. The pores in the micrographs indicate the occurrence of phase separation in the polymer electrolytes [36, 37]. It is concluded that the plasticizer-rich phase shows a homogeneous pore structure, which leads to ion mobility, hence, higher conductivity. It is also observed that the salt, which does not contain any separate phase, confirms the complete dissolution of the salt in the electrolyte medium.

3.5. Lithium transference number

The lithium ion transference number, Li_t^+, is an essential factor which guarantees the performance and high rate capability of lithium batteries for high power applications such as hybrid electric



(a)



(b)

Fig. 5. Chronoamperometric measurements for S_4 sample. Inset: Impedance spectra before and after perturbation.

vehicles [38]. As mentioned in the experimental procedures, the lithium transference number was calculated using equation 1 [20]. The value of Li_t^+ has been calculated as 0.6 which is sufficient for battery applications [39]. Fig. 5a shows the chronoamperometric curve of sample S4 and Fig. 5b shows the Nyquist plots before and after perturbation, respectively. Apparently, both curves (before and after perturbation) overlap, suggesting little difference between the initial (R_0) and the final (R_{ss}) resistances of the two Li interphases, which further confirms the stability of the lithium metal electrode with the chitosan and plasticizers incorporated CGPE.

3.6. Interfacial properties

Lithium is an attractive anode metal with a theoretical capacity of 3862 mAh·g^{-1}. However, its cyclability is limited by dendrite deposition upon recharge. Moreover, lithium is lost in every cycle due to formation of a solid electrolyte interphase (SEI) with the electrolyte. The interfacial properties of lithium metal anodes in contact with the electrolyte are critical in practical applications. In case of polymer electrolyte systems, a resistive layer covers the lithium metal electrode, and the resistance of this layer grows with time, possibly reaching values more than 10 kΩ·cm^{-2} [40]. In the present study, in order to ascertain the interfacial stability of CGPE with lithium metal electrodes, a symmetric cell composed of Li/CGPE/Li was assembled and its interfacial resistance values were measured as a function of time. Fig. 6 illustrates the variation of interfacial resistance, R_i, as a function of time for Li symmetric cells Li/CGPE/Li (with sample S_1 and S_4) at 30 °C. The values of the 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 [41]. The intercept of the large semicircle at high frequency on the Z-axis is mostly associated with the interfacial resistance R_i of the system. The appearance of a small semicircle is due to the charge transfer resistance in parallel with the double layer capacitance.

The interfacial resistance value of the S_1 sample (without plasticizers and filler) increases and decreases in an irregular manner. However, the values of the interfacial resistance of plasticizer and chitosan-added samples are substantially lower than that of the filler-plasticizer free sample. As clearly evident from Fig. 6, the interfacial resistance values for sample S_4 remain more or less the same after 144 hours. This is attributed to the morphological changes in passivated film with time, which is due to the addition of chitosan in the polymeric host as evidenced from Fig. 6.

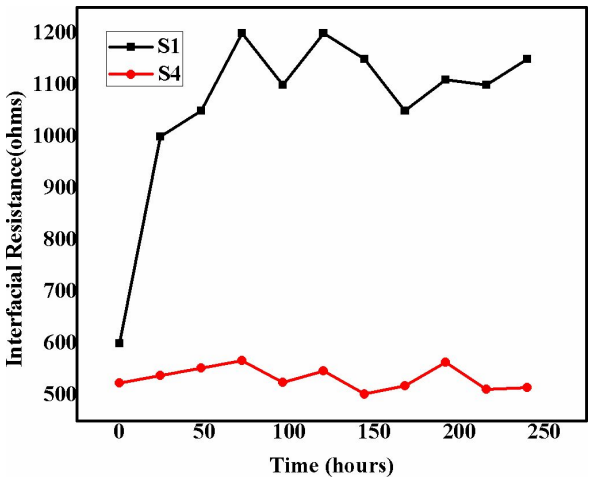


Fig. 6. Variation of interfacial resistance (R_i) as a function of time for samples S_1 and S_4 at 30 °C.

3.7. Electrochemical stability analysis

The electrochemical stability window of the composite gel-polymer electrolyte for the sample S_4 was analyzed using linear sweep voltammetry technique (LSV) and the voltammogram is shown in Fig. 7. It is evident from the current response curve that there is no obvious current passing through the working electrode from the open circuit potential to 5.2 V versus Li^+/Li. The current is observed to flow at 5.2 V which indicates that the CGPE is electrochemically stable up to 5.2 V.

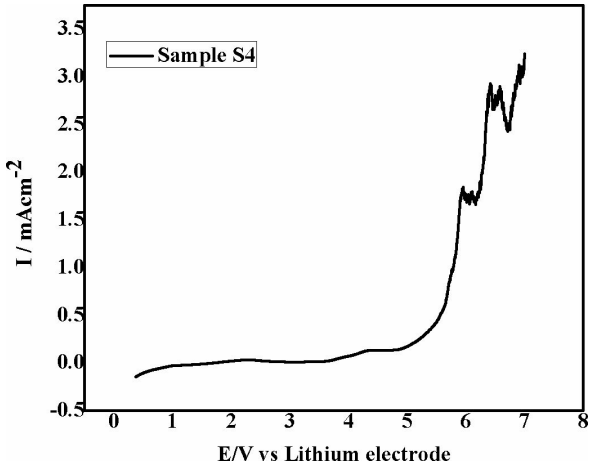


Fig. 7. Linear sweep voltammogram of sample S_4.

The anodic scan showed a very low residual current observed prior to breakdown voltage,

confirming the purity of the synthesized membranes and the synthesizing method we adopted, because the system, as a whole is sensitive to oxygen, water and other impurities.

4. Conclusions

PEO, $LiCF_3SO_3$, plasticizers (DIOX and TEGDME) and chitosan-based composite gel-polymer electrolytes with different content of PEO, chitosan, plasticizer and LiTf were prepared by a simple solution casting method. The complex formation has been confirmed by FT-IR spectral studies. The ionic conductivity was enhanced while adding plasticizer and filler, apparently resulted in increased compatibility between the polymer and plasticizers. On the other hand, conductivity subsequently decreased with increasing plasticizers content. TG/DTA studies confirmed the thermal stability of the electrolyte membrane up to 362 °C. These polymer electrolytes are suitable for lithium battery applications even at high temperatures. The value of interfacial resistance R_i has been found to be lower for chitosan and plasticizers added samples than for filler-free samples under open circuit conditions at 30 °C. The lithium transference number increased upon the incorporation of chitosan to the polymer matrix. From the electrochemical analyses, it can be stated that the gel polymer electrolyte system is an effective tool for improving the properties of lithium polymer secondary batteries.

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