Highly electrochemical stability of PEO-based polymer electrolytes for lithium-metal batteries

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ABSTRACT

Polyethylene oxide (PEO)-based polymer electrolytes, incorporating lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and succinonitrile, are highly promising for solid-state lithium-ion batteries due to their superior ionic conductivity and electrochemical stability. Electrochemical impedance spectroscopy (EIS), electrochemical stability window (ESW) are used in this study to assess the electrochemical performance of the electrolyte system. EIS exhibits ionic conductivities exceeding 10^{-4} S/cm at room temperature because of the plasticizing effect of succinonitrile, which reduces PEO crystallinity, and the enhanced ionic dissociation of LiTFSI. ESW measurements demonstrate a stability window surpassing 4.8 V, enabling compatibility with high-voltage cathodes. GPE-Li3 (MW = 600,000; m_{SN}:m_{PEO} = 0.2; m_{Li}:m_{PEO} = 0.2) exhibits the highest ionic conductivity ($2.79x10^{-4}$ S/cm) and applied voltage up to 4.2 V, can be considered a promising gel polymer electrolyte configuration for lithium metal batteries.

Keywords: Polymer electrolyte; Li-ion batteries; LiTFSI.

1. INTRODUCTION

Lithium metal batteries (LMBs), which use lithium metal as the anode, offer significantly higher energy density compared to conventional lithium-ion batteries (LIBs). However, the performance of LMBs is still limited by two problems: uncontrolled growth of Li dendrite and low Coulomb efficiency during charge-discharge [1]. These two problems originate from many factors, mainly due to instability from ion deposition and the interface between battery components. This will cause hazards such as short circuit or loss of thermal control due to the ability of branched Li to penetrate the separator and low efficiency. While the low Coulomb efficiency can be improved by increasing the Li^+ ion in the electrolyte, overcoming the uncontrolled growth of Li dendrite is much more complicated. The dead Li layer will continuously be generated, which may lead to a short circuit [2]. The growth of Li dendrite is also one of the main reasons for the loss of thermal control in batteries [3]. Therefore, overcoming the problem of Li dendrite growth in LMB batteries is extremely necessary, as it closely affects the application of LMB batteries.

Commercial batteries mainly use liquid electrolyte (LE) as the ion transport medium due to its high ionic conductivity and wettability with electrodes and separators. Solvents are prone to loss, explosion and loss of thermal control due to the development of Li dendrite as mentioned above. Therefore, the solution to manufacture solid electrolytes to replace LE is necessary. Solid electrolytes from polymers or ceramics have been studied extensively; however, they are difficult to widely deploy due to low ionic conductivity (< 10^{-5} S/cm), complex fabrication techniques and poor contact between the solid electrolyte and the electrode.

Gel polymer electrolytes (GPEs) combine the advantages of both liquid and solid electrolytes, offering good ionic conductivity, mechanical robustness, and flexibility. They can mitigate dendrite formation, improve operational stability, and extend cycle life. The properties of Li salts affect the charge/discharge performance of Li-polymer batteries. Organic lithium salts containing sulfonate anions, such as $LiCF_3SO_3$, $LiC_2F_5SO_3$, $LiC_4F_9SO_3$, exhibit high oxidative stability, good thermal resistance, and low moisture sensitivity, but typically have lower ionic conductivity.

Succinonitrile (SN) significantly increases the ionic conductivity in PEO membranes by reducing crystallinity and increasing the number of free ions, while maintaining high mechanical properties [4]. The composite system consisting of PEO-LiTFSI with 5% SiO_2 and 5% SN achieved an ionic conductivity of 3.3×10^{-4} S/cm at 60 °C and the cell exhibited a high initial capacity with end-of-cycle efficiency retention of up to 99% [5]. Although succinonitrile and LiTFSI have been shown to significantly enhance the ionic conductivity of PEO systems, most previous studies reported this improvement only at elevated temperatures, and the practical performance requirements at room temperature have not yet been fully met. Therefore, a systematic study of the PEO/SN/LiTFSI combination is necessary to optimize the GPE performance for safe and sustainable LMB applications.

In this study, GPE based on poly(ethylene oxide) (PEO) was fabricated by using SN plasticizer and LiTFSI salt as the lithium source. The effects of polymer chain length, plasticizer content, and salt concentration on the electrochemical properties of the PEO/SN/LiTFSI complex were systematically investigated.

2. PROBLEM

2.1. Materials

All the reagents, including PEO (M_W = 1 × 10^5, 3 × 10^5, 6 × 10^5, 1 x 10^6, and 2 x 10^6), SN (succinonitrile, 99%), LiTFSI (bis(trifluoromethane) sulfonimide lithium salt, 99.9%), acetonitrile, and dimethylformamide (DMF) were purchased from Macklin suppliers and used without additional purification.

2.2. Preparation methods

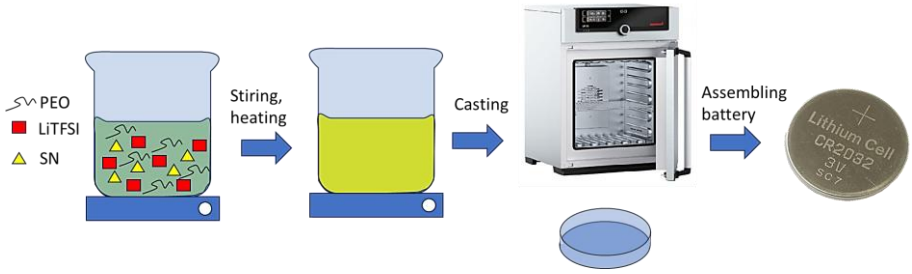

Figure 1. *Manufacturing process of PEO-based gel electrolyte.*

The manufacturing process of PEO-based gel electrolyte was shown in figure 1. PEO, LiTFSI and SN were dispersed in a mixture of acetonitrile and DMF solvents until a homogeneous solution was obtained. The resulting mixture was cast on a PP mold in a vacuum oven for 6 h. Then, the obtained electrolyte was cut and packed into a CR2032 battery for electrochemical properties measurement.

Survey samples according to molecular weight PEO 100,000; 300,000; 600,000; 1,000,000; 2,000,000 respectively: GPE-MW1, GPE-MW2, GPE-MW3, GPE-MW4, GPE-MW5. Survey samples according to SN content m_{SN}:m_{PEO}= 0, 0.1, 0.2, 0.3, 0.4, respectively: GPE-SN1, GPE-SN2, GPE-SN3, GPE-SN4, GPE-SN5. Survey samples according to LiTFSI content m_{Li}:m_{PEO}=0, 0.1, 0.2, respectively: GPE-Li1, GPE-Li2, GPE-Li3.

2.3. Characterization methods

2.3.1. Electrochemical Impedance Spectroscopy (EIS)

EIS is an effective instrument for determining bulk electrolyte and electrode characteristics, investigating interfacial interactions, and evaluating the behavior of full-cell devices. Applied frequency: 10^5 – 0.1 Hz, Number of frequencies: 10 per decade, Temperature: RT, Measurement after assembling for at least 4 h.

For the symmetric stainless steel (SS) cell, the ionic conductivity of GPE is given by [6]:

$$\sigma = \frac{l}{R_b.A} \quad (1)$$

Where σ is the ionic conductivity of GPE (S/cm), R_b is the resistance of electrolyte (Ω), A is the contact area of electrode (cm^2), l is the thickness of GPE (cm). In this study, SS with a diameter of 16 mm, the thickness of GPE can be measured by disassembly of the cell, then measured with a film thickness gauge. R_b is obtained from the Nyquist plot.

2.3.2. Linear sweep voltammetry

Anodic sweep in the SS|SPE|Li cell (Ivium) is measured at the scan rate of 1 $mV.s^{-1}$, from 2 to 6 V, at RT. The current is recorded, and the current-voltage diagram is shown. The on-set point of peak in the diagram is determined as the oxidation potential of SPE, according to the study [7, 8].

3. RESULTS AND DISCUSSION

3.1. Investigation of the effect of PEO molecular weight

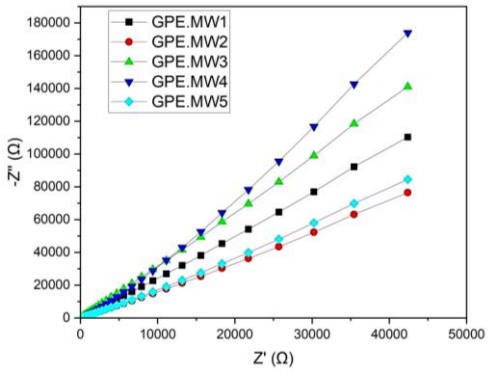

Figure 2. *The Nyquist plot of the cell SS|GPE-MW|SS.*

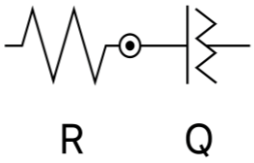

Figure 3. *The equivalent circuit of cell SS|GPE-MW|SS.*

Figures 2 and 3 show the Nyquist plot and the equivalent circuit of GPE-MW1, GPE-MW2, GPE-MW3, GPE-MW4, and GPE-MW5 with symmetrical cell SS|GPE|SS, respectively. From the Nyquist diagram, the linear impedance curves indicate that MW1, MW2 have low resistance, so the ion conductivity is low.

From MW3 to MW4, the resistance decreases and the slope of the linear region becomes steeper, suggesting enhanced ionic conductivity. However, for MW5, the impedance increases again, resulting in a reduction in conductivity compared with MW3 and MW4. The equivalent circuit derived from the Nyquist plot consists of R and Q. R represents the resistance of the polymer electrolyte. Q represents the double capacitance at the interface between the electrolyte and SS.

The calculated ionic conductivity values from R are shown in figure 4. MW3 gives the largest ionic conductivity: 2.75 x 10^{-4} S/cm, consistent with the analytical results in figure 2.

The results indicate that the molecular weight of PEO directly influences both the mechanical properties and the microstructural arrangement of the GPE. At low molecular weight, the polymer chains are too short to form a continuous network, resulting in poor ionic transport pathways. At medium molecular weight, reduced crystallinity promotes amorphous regions that facilitate Li^+ mobility, while sufficient chain entanglement provides adequate mechanical stability, leading to enhanced ionic conductivity. When the molecular weight is excessively high, the polymer tends to form a more optimal amorphous structure that ensures both efficient ion transport and mechanical robustness, thereby yielding the highest ionic conductivity [9].

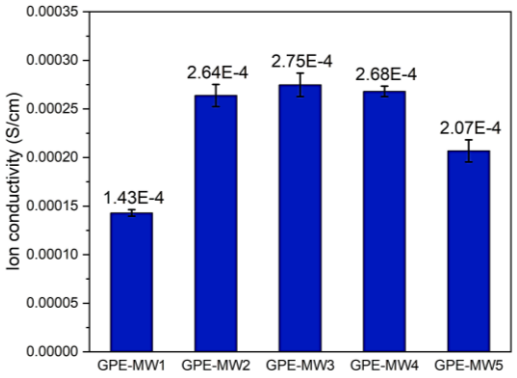

Figure 4. *The calculated ionic conductivity values from R of SS|GPE-MW|SS.*

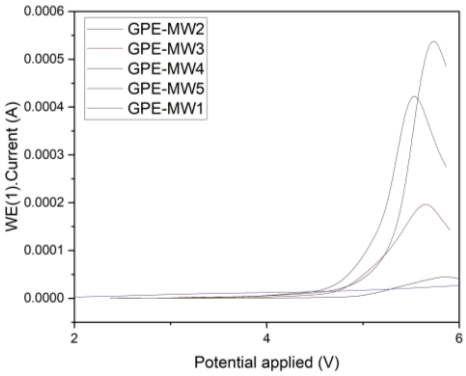

Figure 5. *LSV of cell Li|GPE-MW|SS.*

The LSV results in this work indicate that the electrochemical stability window of the PEO/LiTFSI/SN system ranges from 4.5–5.0 V (figure 5). The electrochemical stability window (ESW) is the range of potentials within which an electrolyte can operate stably without being oxidized or reduced. The presence of SN helps to reduce the crystallinity of PEO, while stabilizing the $TFSI^-$ anion, thereby expanding the electrochemical window to nearly 4.8 V [10]. In contrast, PEO systems with medium Mw (~600k) achieve a balance between ionic conductivity and electrochemical stability, while too high Mw causes a decrease in stability due to the formation of easily oxidized sites [11]. Our results are in full agreement with this trend, as the low Mw samples (MW1, MW2) remain stable up to 5.0 V, but the highest Mw sample (MW5) exhibits an earlier decomposition at around 4.5 V. This demonstrates the important influence of Mw in optimizing the electrochemical window of GPE.

From the above arguments, the GPE-MW3 sample achieved a high ionic conductivity and electrochemical stability window. Therefore, the MW value of 600,000 was chosen for further experiments.

3.2. Investigation of the effect of SN content

EIS and onic conductivity measurements clearly demonstrate the effect of SN content in GPE. The Nyquist plot (figure 6) shows that the resistance value gradually decreases from sample SN1 to sample SN5, except for sample SN2, which has a lower resistance than SN5. In contrast, the ionic conductivity data (figure 7) show that sample SN5 reaches the highest value of 2.77 x 10^{-4} S/cm, which is superior to samples SN1 and SN2. This may be because sample SN2 may have an uneven SN dispersion area, which hinders local ion diffusion. Samples SN3 and SN4 also exhibit quite high ionic conductivities.

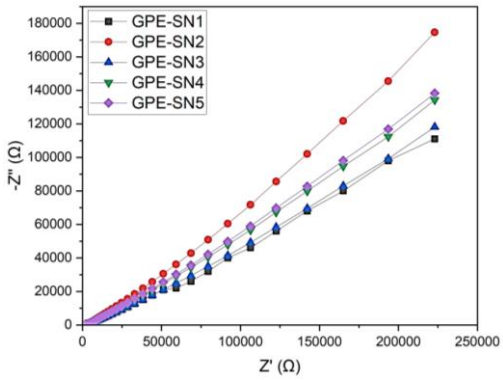

Figure 6. *The Nyquist plot of the cell SS|GPE-SN|SS.*

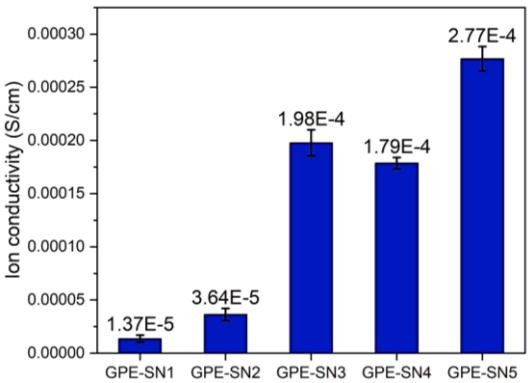

Figure 7. *The calculated ionic conductivity values from R of SS|GPE-SN|SS.*

The LSV plot (figure 9) shows that sample SN1 is susceptible to decomposition at 4.5 - 4.8 V, while samples SN2 to SN5 shift the oxidation threshold higher (5.0 - 5.2 V), which means they are more electrochemically stable. In particular, SN3–SN5 have both high ion conductivity (from EIS) and wide ESW (from LSV), showing better balance properties than SN1–SN2. Although the best sample is SN5, the study still selected sample SN3 because the amount of SN in sample SN5 is twice that of SN3, but the efficiency is not significantly superior to sample SN3.

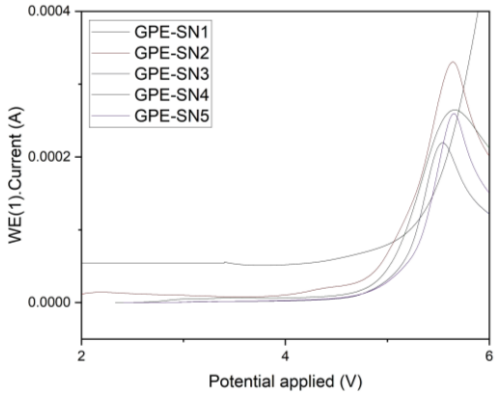

Figure 8. *LSV of cell Li|GPE-SN|SS.*

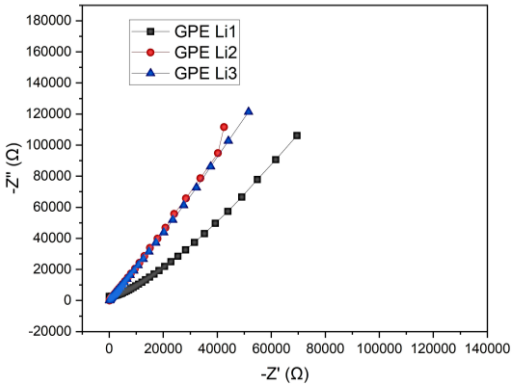

Figure 9. *The Nyquist plot of the cell SS|GPE-Li|SS.*

3.3. Investigation of the effect of LiTFSI content

EIS shows that the impedance changes significantly with the change of Li salt content (figure 9). Specifically, sample Li1 has the highest impedance, samples Li2 and Li3 have lower impedance, reflecting the improved Li ion transport capacity as the mobile ion density increases (increasing salt content). This is consistent with the ion conductivity measurement results, where GPE-Li3 reaches the highest value (2.79×10^{-4} S/cm), surpassing GPE-Li1 (1.43×10^{-4} S/cm) (figure 10). However, this sample has a narrower electrochemical stability window than GPE-Li1 (figure 11). This may be because increasing salt content/changing the polymer structure can facilitate ion transport but at the same time reduce the electrochemical degradation stability [12].

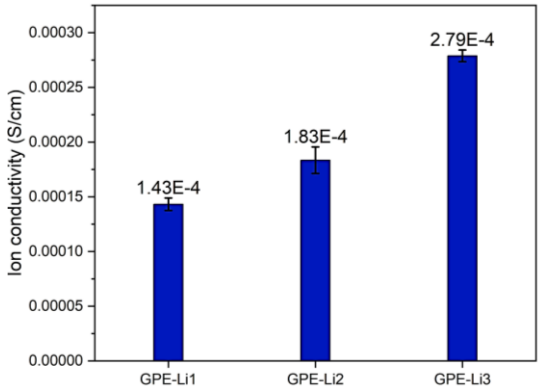

Figure 10. *The calculated ionic conductivity values from R of SS|GPE-Li|SS.*

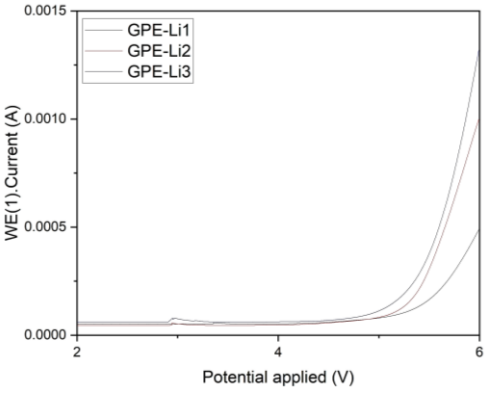

Figure 11. *LSV of cell Li|GPE-Li|SS.*

For applications using GPE that prioritize ion conductivity at room temperature, voltage less than 4.2 V (LFP or NMC), choose Li3 because it has the highest ion conductivity while still meeting the electrochemical stability window. For high voltage cathodes (voltage not less than 4.4V) or if you want to prioritize electrochemical safety, choosing Li1 is necessary. The electrochemical properties of GPE fabricated at the optimized condition.

Overall, GPE-Li3 (MW= 600,000; m_{SN}:m_{PEO}= 0.2; m_{Li}:m_{PEO}= 0.2) exhibits the most favorable balance, combining the highest ionic conductivity ($2.79x10^{-4}$ S/cm) with a sufficiently wide electrochemical stability window (LSV), making it a promising candidate for practical applications at voltages no more than 4.2 V.

Previous studies often targeted single enhancements, such as succinonitrile (SN) or inorganic fillers to improve ionic conductivity, but these efforts commonly resulted in conductivities effective only at elevated temperatures (>40-60 °C) or compromised electrochemical stability. For instance, PEO–LiTFSI–SN systems have achieved conductivities up to ~10^{-3} S/cm at 30 °C but often suffer from poor mechanical integrity or limited electrochemical window (~4.5 V) [13], PEO–LiTFSI–SiO_2–SN composites reach $\sigma \approx 3.3\times10^{-4}$ S/cm but at 60 °C [14].

In contrast, our work presents the first demonstration of simultaneous optimization of the PEO molecular weight, SN content, and LiTFSI concentration, resulting in high room-temperature ionic conductivity (2.79×10^{-4} S·cm^{-1}) and a wide electrochemical stability window (more than 4.2 V). This combination of performance and stability under ambient conditions, suitable for high-voltage battery applications, marks a significant advancement over existing literature.

4. CONCLUSIONS

This study elucidated the combined effects of PEO molecular weight, succinonitrile (SN) content, and LiTFSI salt concentration on the electrochemical properties of polymer electrolytes. Low-molecular-weight PEO enhances chain mobility and thus facilitates ionic transport, but compromises mechanical integrity. In contrast, high-molecular-weight PEO improves structural strength while restricting segmental motion, which reduces conductivity. Increasing SN content lowers interfacial impedance and significantly enhances ionic conductivity by promoting polymer matrix flexibility; however, excessive SN leads to poor electrochemical stability due to its susceptibility to oxidation and reduction at elevated potentials. Similarly, an appropriate LiTFSI concentration provides sufficient free Li^+ ions for effective transport, whereas excessive salt induces ion pairing and clustering, thereby diminishing both ionic conductivity and stability.

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TÓM TẮT

Độ ổn định điện hóa cao của chất điện phân polymer gốc PEO cho pin Lithium kim loại

Chất điện phân polymer gốc polyetylen oxit (PEO), kết hợp lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) và succinonitrile, rất hứa hẹn cho pin lithium-ion thể rắn nhờ độ dẫn ion và độ ổn định điện hóa vượt trội. Nghiên cứu này sử dụng phổ trở kháng điện hóa (EIS) và cửa sổ ổn định điện hóa (ESW) để đánh giá hiệu suất điện hóa của hệ thống điện phân. EIS thể hiện độ dẫn ion lớn hơn 10^{-4} S/cm ở nhiệt độ phòng do tác dụng dẻo hóa của succinonitril, làm giảm độ kết tinh của PEO, và sự tăng cường phân ly ion của LiTFSI. Các phép đo ESW cho thấy cửa sổ ổn định điện hóa đều lớn hơn 4,2 V, cho phép tương thích với catốt điện áp cao.

Từ khoá: Chất điện phân polymer; Pin Li-ion; LiTFSI.