

Effect of the addition of nanosized silica to (PEO)₂₀LiBETI polymer electrolytes

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As a result of wide research over the past few decades, hybrid battery systems using polymer electrolytes are considered one of the most promising candidates for electric vehicle applications. To date, PEO-based polymer electrolytes have been regarded as one of the most suitable for lithium batteries. The PEO-LiX complexes are known to have problems associated with poor mechanical properties and low ionic conductivities at the low temperatures applicable for lithium polymer batteries. To overcome these problems, most efforts have focused on the introduction of inert fillers and lithium salts having large anions into the polymer matrix. The improvement of the ionic conductivity due to the enhanced segmental motion in amorphous regions by the incorporation of inert fillers such as Al₂O₃, SiO₂, TiO₂ and γ -LiAlO₂ has been reported [1-2]. In a previous paper, we have reported that (PEO)_nLiBETI polymer electrolytes have higher ionic conductivities and improved interfacial stability over other solvent-free polymer electrolytes [3-4].

In this study, PEO-based polymer electrolyte was prepared by a solvent-free procedure developed at ENEA in order to exclude the influence of solvents on the ionic conductivity of polymer electrolytes. Aero silica (AS) and fumed silica (FS), composed of nano-size particles, were incorporated into the PEO polymer matrix as inert fillers. The ionic conductivity, interfacial stability, cyclic voltammetry and limiting current density were investigated for (PEO)₂₀LiBETI-10wt% filler polymer electrolytes.

All materials were dried and sieved into fine particles. The materials were mixed and gently ball-milled for 5h with a ratio of ball:sample = 2:1. The ball-milled powders were then hot-pressed at 100 °C to produce polymer electrolyte films less than 100 μ m thick which were then characterized. The active areas of the copper blocking electrodes and Li metal non-blocking electrodes were 4 and 1cm², respectively.

Fig. 1 compares the Arrhenius plots for (PEO)₂₀LiBETI and (PEO)₂₀LiBETI -10wt% filler polymer electrolytes. All of the electrolytes displayed a nonlinear ionic conductivity behavior with temperature during heating and cooling cycles. This indicates that the ionic conduction predominates in the amorphous region. The ionic conductivities of all the samples show similar values which are around 10⁻³ S cm⁻¹ at 100 °C. This indicates that the inert fillers in the PEO-based polymer electrolytes have no influence on the ionic conductivity at high temperatures.

Fig. 2 shows the cyclic voltammetry curves of the (PEO)₂₀LiBETI and (PEO)₂₀LiBETI -10wt% filler polymer electrolytes sandwiched between lithium electrodes. Anodic and cathodic peaks corresponding to lithium stripping and deposition show symmetrical curves. The anodic and cathodic peak currents increased with the incorporation of inert fillers into the polymer matrix. This suggests that a stable passive layer formed on the surface of the lithium electrode due to the reaction with the filler and polymer electrolyte permitting more facile lithium stripping and deposition.

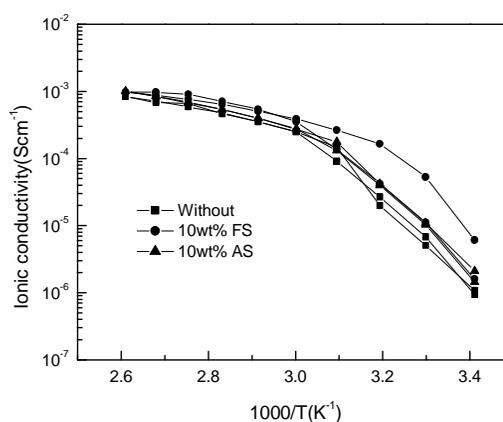


Fig. 1. Arrhenius plots of ionic conductivity of (PEO)₂₀LiBETI and (PEO)₂₀LiBETI-10wt% filler polymer electrolytes sandwiched between copper electrodes.

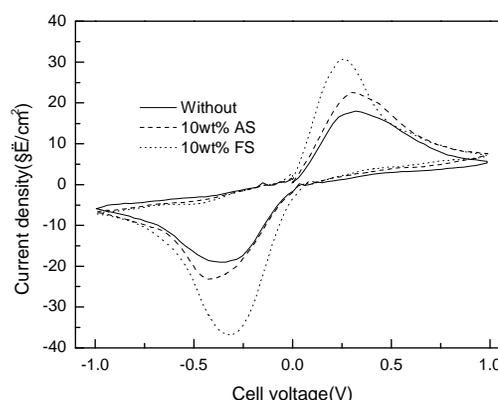


Fig. 2. Cyclic voltammetry of (PEO)₂₀LiBETI and (PEO)₂₀LiBETI-10wt% filler polymer electrolytes sandwiched between lithium electrodes. Sweep rate was 0.1 mV s⁻¹ at 20 °C.

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References

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