

**SYNTHESIS AND CHARACTERIZATION OF SOME PEO-BASED,
NANO COMPOSITE POLYMER ELECTROLYTES**

A THESIS PRESENTED BY

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SYNTHESIS AND CHARACTERIZATION OF SOME PEO- BASED, NANO COMPOSITE POLYMER ELECTROLYTES

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An electrolyte is an essential component of an electrochemical power source. It is a medium with high ionic conductivity and negligible electronic conductivity. From the practical point of view, conventional liquid electrolytes have many drawbacks such as electrolyte leakage, electrolyte corrosion, weight and complex design, leading to a large volume expansion. Owing to their potential ability to replace the traditional liquid electrolytes in electrochemical cells, high molecular weight poly(ethylene oxide) (PEO)-based polymer electrolytes are emerging as the best candidates to be used as polymer electrolytes. Although these electrolytes have high solvation power, complexion ability and ion transport directly connected with alkaline salt (Li^+), their, the ionic conductivity at ambient temperatures (10^{-7} - 10^{-6} S cm^{-1}) is not high enough for most practical applications. In order to overcome this problem, many strategies have been attempted, such as the inclusion of cross-linking agents to form networks, incorporating low molecular weight additives and inorganic fillers. Among these, the incorporation of nano-sized ceramic oxide fillers, to the conventional PEO-salt matrix has been regarded as one of the most promising methods. However, systematic and detailed studies of such nano- composite electrolytes are still lacking.

In the present work, different types of PEO- based nano composite polymer electrolytes have been synthesized using common solvent casting method and characterized them mainly using Complex Impedance Spectroscopy (CIS) and Differential Scanning Calorimetry (DSC). The surface morphology of some selected samples has been studied using Scanning Electron Microscope (SEM).



For the system, PEO: LiTf, the addition of nano- sized alumina fillers have increased the ionic conductivity of the polymer salt complex giving the maximum conductivity enhancement for the samples with 15 wt. % Al₂O₃. The conductivity at 25 °C increased from 3.5x10⁻⁷ S cm⁻¹ to 2.1x10⁻⁵ S cm⁻¹ due to the addition of 15 wt. % Al₂O₃. Incorporating ethylene carbonate (EC) with (PEO)₉LiTf + 15 wt. % Al₂O₃ polymer electrolyte resulted in further increase in conductivity, from 2.1x10⁻⁵ S cm⁻¹ to 1.5x10⁻⁴ S cm⁻¹ at room temperature.

In (PEO)₉LiTf: Al₂O₃: (EC/PC) system, the combined effect of the plasticizer and the filler on ionic conductivity and thermal properties of the polymer electrolyte, (PEO)₉LiTf, have been studied in detailed and the maximum conductivity enhancement was observed for the polymer electrolyte, (PEO)₉LiTf + 15 wt.% Al₂O₃ + 50 wt.% [75% EC+ 25% PC], with a room temperature conductivity value of $\sigma_{RT}(\max) = 1.2 \times 10^{-4}$ S cm⁻¹.

In the system, (PEO)_nLiBF₄ (n = 3, 6, 8, 10, 12, 15, 20), the composition, n = 12, showed the highest conductivity of 8.7x10⁻⁶ S cm⁻¹ at the room temperature (25 °C) among different Li / EO ratios. The addition of nano- porous alumina filler to this electrolyte (with n = 12) increased the ionic conductivity of the polymer salt complex giving the maximum conductivity enhancement for the sample with 15 wt. % Al₂O₃ [$\sigma_{RT}(\max) = 6.1 \times 10^{-5}$ S cm⁻¹].

The ionic conductivity enhancement due to the incorporation of filler is evidently associated with the surface interactions of the filler with ionic species. One possible mechanism is the creation of favorable conducting pathways through Lewis acid-base type interactions of ionic species with O/OH surface groups on filler grains. The effect of filler on T_g suggest that the filler particles interact with main chain dynamics of the host polymer presumably through Lewis acid-base type interactions between the ether oxygen and filler surface groups leading to a lowering of the T_g. The filler also impedes crystallization and increases the amorphous phase content of the polymer electrolyte. Therefore, it is evident that a major contribution to the conductivity enhancement comes from the structural modifications associated with the polymer host caused by the filler.