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Plasticized and plasticizer-free, Nano- composite polymer electrolytes for rechargeable Li –ion batteries

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One of the major drawbacks in PEO - LiX polymer electrolytes is the low ionic conductivity at ambient temperatures. The most promising methods to overcome this problem are the incorporation of ceramic fillers, as was first suggested by Weston and Steele (1982) and the incorporation of organic plasticizers to the polymer electrolytes. However, the incorporation of plasticizers alone will yield polymer electrolytes with poor mechanical properties. In our recent work, we studied the dependence of ionic conductivity on different types of ceramic fillers and also the effect of incorporation of plasticizer and ceramic filler together in PEO LiTf polymer electrolytes. In this work, we have studied thermal and electrical properties of the polymer electrolyte PEO_9 LiTf + 15 wt% filler, incorporating four different types of ceramic fillers TiO_2, Al_2O_3, ZrO_2 and $BaTiO_3$. We have also studied thermal and electrical properties of PEO_9 LiTf EC : Al_2O_3 polymer electrolyte incorporating Ethylene carbonate (EC) as the plasticizer. In the first system, the presence of the first three ceramic fillers with dielectric constants 435, 20 and 12.5 enhanced the ionic conductivity substantially. However $BaTiO_3$ filler having a relatively very high dielectric constant (3000) compared to other three ceramic fillers has resulted in a drop in conductivity. Presence of 15 wt% TiO_2 exhibited the maximum enhancement in conductivity ($\sigma_{RT} = 4.2 \times 10^{-4}$ S cm $^{-1}$). The observed conductivity enhancement has been attributed to Lewis acid-base type surface interactions of ionic species with O/ OH groups on the filler surface. In the second system, it was observed that the addition of plasticizer (EC) to the PEO_9LiTf + 15 wt% Al_2O_3 electrolyte up to a concentration of 50 wt. %, showed a maximum conductivity enhancement [$\sigma_{RT} = 1.5 \times 10^{-4}$ S cm $^{-1}$]. It is suggested that the conductivity is enhanced mainly by two mechanisms. The plasticizer (EC) would directly contribute by reducing the crystallinity and increasing the amorphous phase content of the polymer electrolytes. The ceramic filler (Al_2O_3) would contribute to conductivity enhancement by creating additional sites to migrating ionic species through transient bonding with O/OH groups in the filler surface. The decrease of T_g values of plasticized composite polymer electrolyte systems seen in the DSC thermograms points towards the improved segmental flexibility of polymer chains giving rise to increased mobility of conducting ions.

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