ABSTRACT

Since the last few decades, the research on the development of ion-conducting materials has been expanding due to their interesting and wide variety of applications in electrochemical devices such as batteries, supercapacitors, fuel cells, sensors, electrochromic display devices, etc. Ion conducting materials which exhibits high ionic conductivity of the order of ~ 10^{-5}-10^{-1} S cm^{-1} and negligible contributions from electrons which is also termed as 'Fast Ion Conductors' or 'Superionic Solids'. Based on the microstructure and physical properties, the ion-conducting material is classified as framework crystalline/polycrystalline solid electrolyte, glassy/amorphous Solid Electrolytes, composite solid Electrolytes, polymer-based electrolyte. Among these, polymer-based electrolytes have received much attention over another ion-conducting electrolyte due to ease of fabrication, free from leakage, and good electrode-electrolyte contact. The polymer electrolytes, developed so far, are classified as solvent-free polymer salt complexes or dry solid polymer electrolytes, plasticized polymer electrolytes, rubbery polymer electrolytes, gel polymer electrolytes, composite polymer electrolytes. Solid polymer electrolytes can be formed by dissolving salt into high molecular weight polymers such as PEO, PPO, PVA, etc.

The conventional solid polymer electrolytes (polymer-salt complexes) possess very low ionic conductivity because ion transportation through PE is governed by polymer chain segmental motion as well as local relaxation which is not possible in the partially crystalline PE. For that, a high degree of amorphicity in polymer electrolytes is required. Alternatively, the gel polymer electrolyte system has been found as a potential candidate due to the possessor of high ionic conductivity of the order of 10^{-4} to 10^{-3} S cm^{-1}. Apart from it, other few interesting points are no leakage like a liquid electrolyte, easy to prepare, and shaped it in the form of thin-film, no degradation, high compatibility with electrodes, high energy density, etc. Gel polymer electrolytes (GPEs) are usually obtained by incorporating a large amount of organic liquid solvents/plasticizers such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), etc. into a polymer matrix which enhances the amorphous nature of the polymer and softens the polymer backbone resulting in high segmental motion of polymer chains and assists the easy movement of ions through the polymer matrix But, due to presence of a large amount of plasticizers, the mechanical strength becomes poor which is not suitable with the electrodes. To improve the ionic conductivity and mechanical strength, the researchers have adopted a few methods to such as blending, adding nanoparticles, and crosslinking, etc. One of the pragmatic and simplest approaches is to the dispersion of nanofillers (inert insulating ceramic filler) such as SiO_2, TiO_2, ZrO_2, $BaTiO_3$ into the polymer matrix.

Keeping in mind, the above facts, in the present work, the gel polymer electrolytes have been prepared which is comprised of poly (vinylidene fluoride hexafluoropropylene) PVDF-HFP and poly (methyl methacrylate) PMMA as host polymers, $LiClO_4$ salt as an ion-conducting species, Propylene carbonate (PC) and diethylene carbonate (DEC) as plasticizers, and Al_2O_3 as nano-filler. The PVDF-HFP is a semicrystalline polymer that possesses both amorphous and crystalline phases in which the amorphous HFP part can trap large amounts of liquid electrolytes whereas the crystalline VDF part assists in the improvement of the mechanical stability and PMMA is blended with it owing to its amorphous nature which aids in increasing the amorphicity. A mixture of PC and DEC is taken owing to its high dielectric constant and lower viscosity, respectively, and Al_2O_3 nanoparticles are used as filler owing to its high surface to volume ratio and high dielectric constant.

The present study aims to study the properties of the gel polymer electrolyte system for the Li^-ion battery application. The main objective of the present thesis is "***Electrochemical properties of nano-composite polymer blend gel electrolytes for battery applications***"

Prepared series in the current study are:

Series (a): PVDF-HFP:PMMA -PC:DEC (1:1)- x wt.% $LiClO_4$, where x = 2, 4, 5, 7.5, 10

Series (b): PVDF-HFP:PMMA - 10 wt.% $LiClO_4$- x wt.% PC:DEC (1:1), where x = 20, 30, 40, 50, 60

Series (c): PVDF-HFP:PMMA – 10 wt.% $LiClO_4$- 60 wt.% PC:DEC (1:1)- x wt.% Al_2O_3, where x = 0.5, 1, 2, 3, 4

To prepare the gel polymer electrolyte membrane, a typical solvent casting technique has been adopted. Various properties of the prepared gel polymer electrolytes such as structural, morphological, thermal and mechanical, electrical, and electrochemical have been investigated. The battery fabrication is undertaken and their performance is evaluated by measuring open-circuit voltage (OCV) and discharge characteristics at no load and constant load respectively.

XRD is adopted to investigate the structural information. The X-ray diffraction study to understand the increase or extent of amorphicity due to the addition of $LiClO_4$ salt, the addition of PC:DEC plasticizers, and dispersion of Al_2O_3 nanofillers. X-ray diffraction studies confirm the amorphous nature of the optimized gel polymer electrolytes. Fourier transform infrared spectroscopy (FTIR) is carried out to identify the nature of bonding or complex formation after blending polymers, the addition of salt, plasticizers, and nano-fillers, and finally to understand the functional group present in samples. The result of FTIR shows that the complex formation and strong interaction between the present constituents in the gel polymer electrolytes. The thermal analysis of all gel polymer electrolytes is studied by Differential scanning calorimetry (DSC). The results show the lowest melting temperature for the high conducting sample. Surface morphology and surface roughness measurement is carried out using scanning electron microscope (SEM) and atomic force microscopy (AFM). SEM of optimized gel polymer electrolyte shows the presence of uniformly distributed pores filled with a liquid electrolyte which provides a better conducting path for the movement of ions. From AFM analysis, minimum roughness has been observed for the optimum gel polymer electrolyte. The total ionic transport number has been investigated by Wagner's DC polarisation technique is found to be ~ 0.96-0.99 which indicates the present gel polymer electrolyte is the ionic conductor. Estimated transport numbers suggest the charge transport is predominantly ionic. CV is performed to evaluate the electrochemical stability window of the present gel polymer electrolyte system. The tensile strength has been measured to investigate the mechanical properties and upon the addition of plasticizers and nanofiller, the mechanical strength has been improved.

Electrochemical impedance spectroscopy is performed in the frequency range from 1 Hz to 32 MHz in the temperature range 303 K- 348 K to investigate the electrical properties of the GPE system. The temperature-dependent ionic conductivity follows the Arrhenius relationship which indicates that ion hopping in the polymer matrix. AC conductivity, dielectric, and modulus studies were carried out to understand the ion transport properties and relaxation mechanism in the polymer electrolytes. The AC conductivity at a higher frequency region obeys a Jonschers power law. The scaling of AC conductivity for all the samples at different temperatures follows the time-temperature superposition principle. The electrical modulus is studied to understand the electrical relaxation processes which are of the non-Debye type.

Li-ion conducting primary battery using optimum gel polymer electrolyte has been fabricated and discharge characteristics are studied at different loads of 4.8 KΩ, 10 KΩ, 21 KΩ. The cell parameters like open-circuit voltage, discharge capacity, energy density, and power density are calculated.