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Physical and charge discharge behavior of facile PVDF-HFP nanocomposite microporous polymer electrolyte for lithium ion polymer batteries

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ABSTRACT

Synthesized wurtzite ZnO nanostructures are incorporated on the poly (vinylidenefluoride-co-hexafluoropropylene) (PVdF-HFP) matrix, which improves the thermal as well as porosity nature of as obtained thin film nanocomposite microporous polymer membrane (nanoCMPM). The membrane shows a favorable effect on the crystallinity (X_c) of 26.83% and melting temperature (T_m) of 142.9 °C that improves the conductivity of polymer electrolytes. Its characteristics were examined by thermal studies. The optimized polymer membrane was found to have a high degree of porosity (76%) and excellent film strength. The membranes were prepared as a polymer electrolytes in soaking lithium percholoride ($LiClO_4$) salt solution and ethylene carbonate (EC) as well as dimethylene carbonate (DMC) in 1: 1 (v/v) ratio as plasticizer to form gel type nanocomposite microporous polymer electrolytes (nanoCMPE). It shows the ionic conductivity in the order of 10^{-3} S cm^{-1} at 298 K for all optimized polymer electrolytes with different lithium salt electrolyte concentrations. The polymer membrane electrolyte has good compatibility and fabricates [$LiCoO_2$/PVDF-HFP-ZnO-$LiClO_4$/mesocarbon microbeads (MCMB)] as coin type cell. The charge–discharge characteristics as well as cell performance were investigated at 0.5 C rate. The polymer electrolyte is a better candidate to perform in lithium ion polymer batteries.

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1 Introduction

The present generation, rechargeable lithium-ion batteries (RLIBs) are an ideal candidate and showed greater potential applications as energy sources for portable electronic devices, hybrid electric vehicles (HEV), and large-scale energy storage devices [1, 2]. RLIBs are facing different challenges between electrodes and/ or electrolytes. Among these, electrolyte/separator plays a key role to avoid electrical short circuits and rapid transport of ionic charge carriers [3]. Generally, conventional liquid electrolyte has employed and faced many demerits such as leakage, electrochemical instability [4] and short circuit, etc. To overcome this issues, alternative electrolytes such as polymer electrolyte has attracted extensive attention which is widely employed in the rechargeable batteries. It has been prepared in various forms such as solid [5, 6], gel [7, 8], composite [9–11] polymer electrolytes to improve their properties. Polymer electrolytes has chosen due to high energy density, high output voltage, long cycling, low self discharge, high thermal stability, good mechanical property, compatibility between electrodes, and many more [12, 13]. Therefore, a variety of polymer matrix/electrolytes has been employed such as poly(vinylidene fluoride) PVdF [14], poly(methacrylate) PMMA [15], Polyethylene oxide PEO [16], poly(vinylidenefluoride-co-hexafluoro propylene) (PVDF-HFP) [17–19], polyacrylonitrile (PAN) [20] and poly(acrylonitrile-methacrylate) P(AN-MMA) [21] matrix. Among the various available polymer matrices, the copolymer of poly PVDF-co-HFP matrix has received prime significance as polymer electrolytes in lithium batteries [22, 23]. PVdF-HFP polymer electrolyte is used in the most commonly commercialized plastic lithium-ion batteries (PLiONTM) by Telcordia Technologies (formerly Bellcore). Further, Gozdz et al. found the preparation process of the PVDF-HFP porous film [24, 25]. Porous polymer matrix plays a key role in polymer electrolytes, thereby increase the uptake of liquid electrolytes [26]. Meanwhile, micro porous polymer membrane is only preferred but not preferred too large size porous structure, it may be internal short circuit, reduce the mechanical and also electrochemical properties. Hence, to prove the performance, researchers concentrated to prepare nanocomposite polymer membrane electrolytes with addition of fillers such as SiO_2 [27, 28], rutile TiO_2 [29], nano TiO_2 [30] Al_2O_3 [31], MgO [23], ZnO [28]. Among these, zinc oxide has chosen as nanofiller, it is most abundant material after iron. It is inexpensive, safe, thermal, and electrical stability in nature. The addition of nanofillers on PVDF-HFP based polymer matrix has been adopted by phase inversion techniques [32, 33] to obtain the composite microporous membrane and followed by absorption of electrolyte (Lithium salt solution) to reduce the leakage, increase solution uptake and better compatibility towards electrodes [34–37]. $LiClO_4$ salt has selected in view of the fact that smaller in ionic radius, dissociation energy, and easily soluble in organic plasticizers [38]. Therefore, the technical enhancement of the electrolyte as well as separator is immediately wanted to meet the safety requirement for large-scale applications of RLIBs.

This present research study aim is to enhance the thermal, structural, and electrochemical behavior of gel-type nanocomposite polymer electrolyte system. Thus, (a) wurtzite ZnO nanofiller was synthesized by polyol mediated solvothermal process [19]. (b) nanocomposite polymer membrane has prepared with different wt% (x = 2, 4, 6, 8, 10) of ZnO nanofiller incorporated on the PVDF-HFP polymer matrix by phase inversion process. (c) The polymer membranes have been activated by drenching in $LiClO_4$ electrolyte solution to obtain facile gel type nanoCMPE. The nanocomposite polymer electrolytes have suppressed the ignitability of plasticizer. Further, effect of lithium salt concentration on ionic conductivity has been analyzed. The nanocomposite polymer membrane systems were characterized by differential scanning calorimetry (DSC), X-ray diffraction (XRD), and field emission scanning electron microscopy (FE-SEM). Further, the optimized polymer electrolytes are allowed to investigate electrochemical, and charge/discharge behavior by the fabrication of (MCMB/nanCMPE/$LiCoO_2$) coin type cell.

2 Experimental sections

2.1 Materials

The host poly(vinylidenefluoride-*co*-hexafluoropropylene) (PVDF-HFP) [Mw = 500000], and lithium perchloride ($LiClO_4$) as an inorganic lithium salt were obtained from Aldrich (USA) and were dried at