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CSIR-AMPRI

Synthesis and characterization of nanocomposite polymer electrolytes dispersed with ZnO nanoparticles for electrochemical applications

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Abstract : Herein, a new class of nanocomposite polymer electrolyte (NCPE) for electrochemical device applications through solution cast technique has been synthesized by using Polyvinylidenefluoride (PVDF) as a host polymer and characterized. NCPEs consist of polymer electrolytei.e. 70PVDF:30$MgCl_2$ (σ ~ 0.98x10-6S/cm) as phase –Ist and nanoparticles of ZnO as phase-IInd dispersoid. Complex formation in NCPE wasconfirmed by X-Ray Diffraction (XRD) technique. Impedance Spectroscopic technique wasused to study transport properties of NCPEs. 70PVDF:30$MgCl_2$:3ZnO has highest conductivity σ~0.87x10-4 S/cm at room temperature. Wagner's dc polarization technique was used for ionic transport number measurement.Discharge characteristics of prepared films were plotted by fabricatingelectrochemical cellsand various cell parameters have been calculated. The reduction in crystallinity was confirmed by XRD studies. These studies suggested this system of NCPE with ZnO nanoparticles for practical realization of Mg batteries.

Keywords: Transport number;Nanocomposite polymer electrolyte;XRD; Impedance Spectroscopy;Discharge characteristics;

Introduction

The increasing global energy crisis and the hazardous impact on the environment by the use of fossil fuels to produce energy is the main concern of the modern world. [1-18] Magnesium ion conducting solid nanocomposite polymer electrolyte (NCPE) materials used for electrochemical device application (electrochemical display, battery, sensors fuel cells and supercapacitors) have the potential to simultaneously curb the energy and environment related problems by generating electricity from chemical energy without releasing any environment damaging gases.[18] Among the various families of solid electrolyte materials, nanocomposite polymer electrolytes have gained the reputation of being the efficient electrolyte material near room temperature. Some polymer electrolytes reported by various researchers are-Methyl Metha Acrylate-Acrylic acid-LiTFSI based polymer electrolyte by Chen et al. (2021) with ionic conductivity of 3.19×10-3S/cm. [19] Aziz et al. reported Chitosan based polymer electrolyte with composition Chitosan-Methylcellulose NH_4NO_3 has conductivity of 1.31×10-4S/cm. [20] Aziz et al. reported magnesium ion conducting polymer electrolyte (2021) with composition i.e. Chitosan- $Mg(CH_3COO)_2$ –Ni with conductivity ~1.09×10-4S/cm. [21] Zhang et al. (2021)[22] reported a gel polymer electrolyte prepared by sol-gel technology for electrochromic display devices (ECD) with composition polypropylene glycol bis(2-aminopropyl ether) (2-APPG), pyromelliticdianhydride (PMDA), glycidoxypropyltrimethoxysilane(GLMO), and 3-isocynatepropyltriethoxyslane (ICS). This GPE overcomes the problem of thermal stability, low conductivity of electrolytes and shows good electrochemical stability, cycle performance and excellent colouration efficiency.

Al_2O_3 dispersed nanocomposite polymer gel electrolyte reported by Tripathi et al.(2021) prepared by using solution casting technique have composition PVDF-HFP: tetraethylammoniumtetrafluoroborate: EC/PC: Al_2O_3 with the highest conductivity 6.0×10-3 S/cm, ionic transport number (tion) ~0.98 and electrochemical window of ~3.4V.[23]Green polymer electrolyte reported by Nandhini D et al. (2021) 40:20:35:5 wt% of Pectin: Guar: Gum: $MgCl_2$: EC based 0.94 transport number with maximum conductivity 2.71×10-3 S/cm.[24]

In our work, solution casting method was used for synthesis of nanocomposite polymer electrolytes, having PVDF as host, $MgCl_2$as ionic salt and ZnO

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nanoparticles as filler.[6] Zinc oxide nanoparticles are active fillers – can participate in ion conduction, enhances ionic conductivity and electrochemical stability of solid polymer electrolyte (SPE). [1]

In our previous work, we have reported the synthesis and characterization of PVDF: $Mg(NO_3)_2$:MgO [6] polymer electrolyte system and in this work we continue with different series of polymer electrolytes for comparative study of electrolytes having composition 70PVDF: $30MgCl_2$: x wt.% of ZnO nanoparticles with high conductivity values.

Experimental

The polymer Polyvinylenefluoride (M.W.~530000), ionic salt– magnesium chloride(M.W.~203.3)and ZnO (size of nanoparticles ~50nm, M.W. ~ 81.38, Aldrich) were used as raw materials for preparationof polymer electrolytes. Solution casting method was used for synthesis.70PVDF: $30Mg(NO_3)_2$: 3MgO system was prepared by the same process reported elsewhere. [6] All prepared samples of solid polymer electrolyte were named as S_0, S_1, S_2, S_3 and S_4 for Pure PVDF, 10,20, 30 and 40 wt% of salt in PVDF respectively, while samples of nanocomposite polymer electrolyte(NCPE) were named as ZnO 1%, ZnO 2%, ZnO 3% and ZnO 4% for 1, 2, 3 and 4 wt% of ZnO nanoparticles dispersed in optimum conducting composition of solid polymer electrolyte (SPE)i.e. 70PVDF: $30MgCl_2$.

Nanocomposite polymer electrolytes were characterized by XRD (Bruker, D8 Advance X-ray diffractometer), Scanning electron microscopy (NOVA NANOSEM 450 FEI) and Impedance Spectroscopy (HIOKI, model no. 3532-50, LCR Bridge) for structural and ionic conductivity analysis. DC polarization method was used for ionic transport number measurement by fabricatingelectrochemical cell.polarization method variouscell parameters like– OCV, energy and current density,were also calculated from discharge characteristics.

Results and Discussions

Ionic Conductivity measurements

Fig. 1 shows the variation of ionic conductivity of solid polymer electrolyte as a function of different weight percent of salt concentrations. It is observed from figure 1 that 30 wt % of $MgCl_2$ in pure PVDF system has highest conductivity value calculated from conductivity relationship (σ =l/ARb, where l- thickness, A- cross section area andRb – bulk resistance of polymer electrolyte film) is 0.98×10^{-7} S/cm. Fig. 2 gives variation of ionic conductivity of NCPE as a function of ZnO nanoparticles concentrationsin 70PVDF: $30MgCl_2$ polymer electrolyte, to enhance solid polymer electrolytes conductivity value. The highest ionic conductivity value is observed for 3 wt % of ZnO in 70PVDF: $30MgCl_2$nanocomposite polymer electrolyte system(0.87×10^{-4} S/cm). It is observed from XRD results that 3 wt % of ZnO in 70PVDF: $30MgCl_2$ system is most amorphous so have conductivity value that matches our conductivity results. [9]

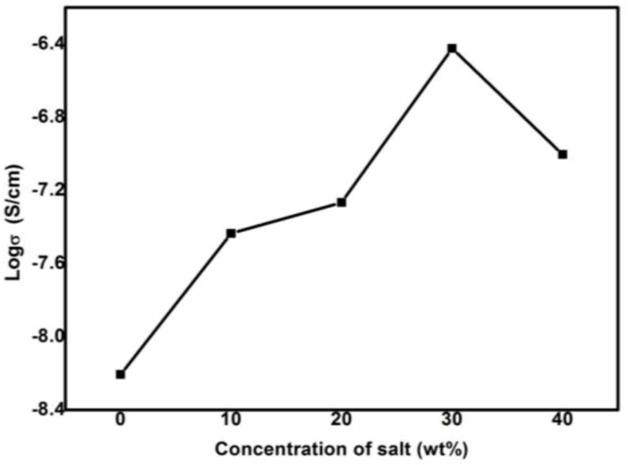

Fig. 1.Variation of ionic conductivity of SPE thin films as a function of salt concentrations ($MgCl_2$) in PVDFat room temperature.

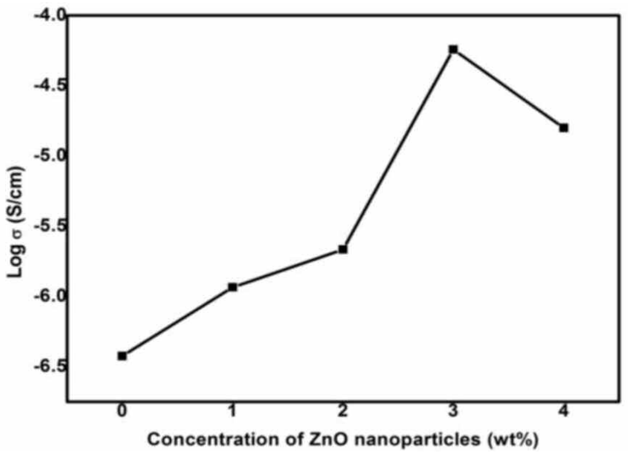

Fig. 2.Variation of ionic conductivity of NCPE thin films as a function ZnO nanoparticles concentrations in 70PVDF: $30MgCl_2$ at room temperature.

XRD study

Fig. 3shows the XRD spectra of prepared solid polymer electrolyte i.e.70PVDF: $30MgCl_2$ and NCPE dispersed with different concentrations of ZnO nanoparticles in solid polymer electrolyte. From XRD spectra of different NCPE films, we observed that a broad peak around 20.3° of PVDF was found to decrease in intensity and peaks at 31.73°, 34.4°, 36.2°, 46.4° and 57.8° are appeared in NCPE films due to dispersion of ZnO nanoparticles, confirms formation of complex.

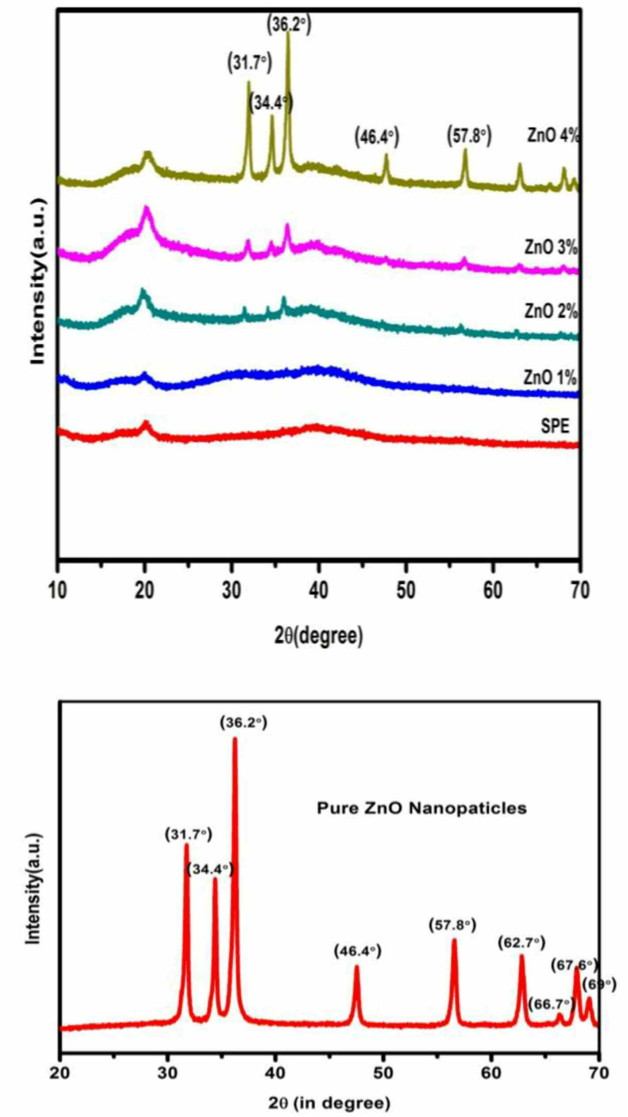

Fig. 3.XRD spectra of a) solid polymer electrolyte i.e.70PVDF: 30MgCl2 and NCPEs with different concentrations of ZnO in SPE and b.) pure ZnO Nanoparticles.

Transport number studies

The ionic (tion) transport number of NCPE has been calculated using dc polarization technique [42]. The tion value obtained from Fig. 5for NCPE with composition (70PVDF:30MgCl2:3ZnO) is 0.99, which is approximately 1. This indicates that charge transport in these electrolyte cells was due to ions this confirms electrolyte in ionic. Fig. 5 shows that the polarization current at the beginning is highest but as time goes on the current decays immediately and asymptotically approaches a steady state.

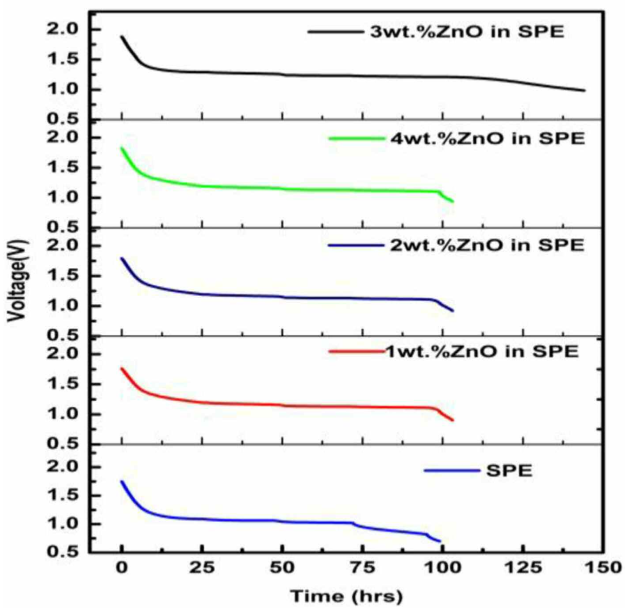

Fig. 5. DC polarization curves of solid polymer electrolyte and NCPE dispersed with different weight percent of nanoparticlesin OCC of SPE in cell configuration Mg| SPE/NCPE| C cell.

Discharge Studies

Discharge characteristics ofsolid polymer electrolyte and nanocomposite polymer electrolyteswere obtained by fabricating electrochemical cellsin cell configuration Mg|NCPE|C-cell (C+I2+electrolyte, 5:5:1) and by discharging this cell at 100kΩ. It was observed from figure 6 that an initial sharp decrease in voltage with time may be due to polarization or formation of a thin layer of magnesium salt at electrode-electrolyte interface. [42]. Forour optimum system, 70PVDF:30MgCl2:3ZnO cell parameters are- OCV~1.85V, Discharge time~ 100hrs, energy density~ 33Wh/Kg and power density~ 0.33W/Kg etc.

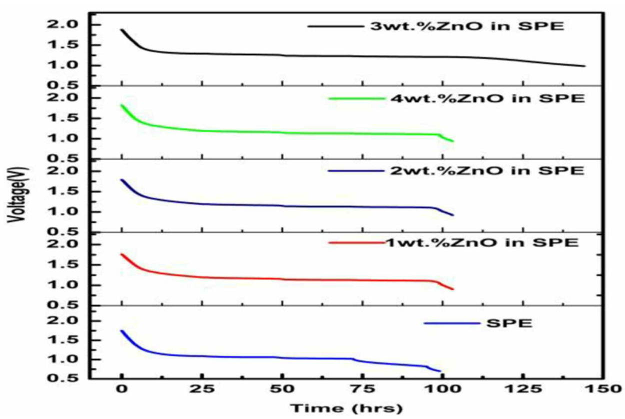

Fig.6. Discharge characteristic of solid polymer electrolyte and NCPE dispersed with different weight percent of nanoparticles in SPE.

SEM Study

Figures 7(a and b) show scanning electron microscopy (SEM) images of pure PVDF, Pure ZnO nanoparticles and Nanocomposite polymer electrolyte. From the SEM image of ZnO nanoparticles, it was observed that nanoparticles havesizes less than 50nm. The SEM used in our study is Field emission scanning electron microscope (FESEM). From surface morphology data it was observed that amorphous nature of polymer was increased on adding nanoparticles into it which is in good agreement with XRD results.

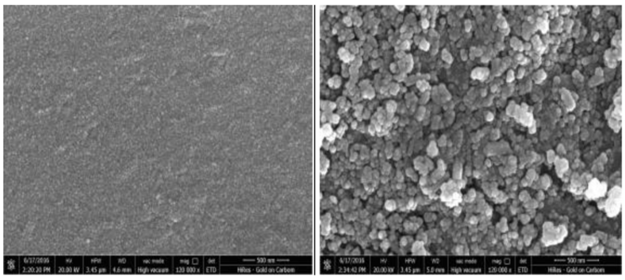

Fig. 7(a).Scanning electron microscopy images of Pure PVDF and Pure ZnO.

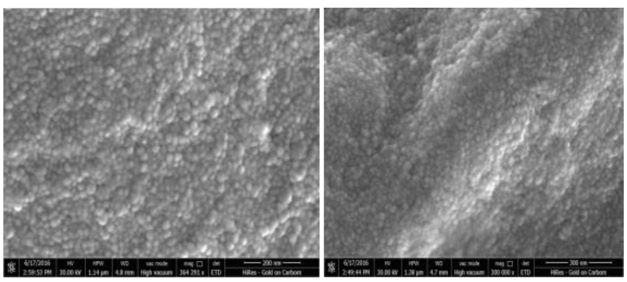

Fig. 7(b).Scanning electron microscopy images of nanocomposite polymer electrolyte atdifferent resolutions.

Conclusions

A new system of nanocomposite polymer electrolyte (70PVDF: $30MgCl_2$: 3ZnO)has been prepared by solution casting technique. The XRD results confirm formation of complex. 70PVDF: $30MgCl_2$: 3ZnO system has highest ionic conductivity σ i.e. 0.87×10^{-4} S/cm at room temperature this indicates that this system has good ionic conductivity. The transport number measurement data gives t_{ion} ~0.99 confirming ionic nature of electrolyte. From electrochemical cell analysis of all these systems, suggests that this system can be a candidate for future electrochemical applications.

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