www.sphinxsai.com

ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.3, pp 1870-1872, May-June 2014

ICMCT-2014 [10th – 12th March 2014]
International Conference on Materials and Characterization Techniques

The structural, vibrational and electrical properties of lithium ion conducting plasticized (PVdF-HFP)/PEMA blend

P.Senthil kumar[1], A.Sakunthala[1,]*, P.Issac Nelson[1], M.Prabu[2]

[1]Department of Physics, Karunya University, Coimbatore 641114, India.
[2]Dept of Energy Systems Engineering, Daegu Gyeongbuk Institute of Sci & Tech, South Korea.

***Corres.author: meetsaku@gmail.com, sakunthala@karunya.edu**

Abstract: The plasticized polymer PVdF-HFP was taken as the host and blended with 5 wt % of PEMA. The effect of blending with respect to structural, vibrational and electrical properties was studied. Blending PEMA with plasticized polymer PVdF-HFP was found to successfully enhance the film flexibility and conductivity. The dielectric spectra show an increase in side chain movement after blending.
Keywords: PVdF-HFP, PEMA, blending, FTIR, conductivity.

Introduction and Experimental

Rechargeable lithium ion batteries (LIB's) are the source of power for any kind of modern electronic good. This is solely due to their high energy density when compared to other batteries like lead acid, Ni-MH, Ni-Cd etc. The first LIB was introduced by SONY in 1991, using $LiCoO_2$ and graphite as cathode and anode, respectively. Organic solvent was used as the electrolyte. From then the research started to bloom in different directions to enhance the energy density, power density and safety of the battery in order to meet the demands of the electronic industry. Polymer electrolytes were found to be a good replacement for organic electrolytes in overcoming safety issues. Good ionic conductivity, mechanical stability, thermal stability, electrochemical compatibility is expected out of a good polymer electrolyte. In this sense, gel polymers, polymer nanocomposites, polymer blends are different ways to achieve the above properties. In the present study, the effect of blending 5 wt% of PEMA with plasticized PVdF-HFP polymer has been investigated. The polymer PVdF-HFP chosen for the present study contains both amorphous HFP and crystalline PVdF phases which provide flexibility and mechanical strength, respectively making it suitable for battery application. Both in PVdF-HFP and PEMA, the polymer salt complex could be easily formed due to the presence of electron pairs at the oxygen atoms of C=O and C-O-C_2H_5, in case of PEMA and at fluorine atoms in case of PVdF-HFP. Hence it would be quite interesting to study the blend effect of above two polymers. Ulaganathan et al [1] has reported on the blending effect of 5 wt% of PEMA in the polymer PVdF-HFP plasticized with plasticizer propylene carbonate (PC) using tetrahydrofuran (THF) as the solvent. The structure of the polymer PVdF-HFP varies depending on the solvent used and solvent evaporation temperature [2]. This will affect the electrical properties of the polymer film. Here we report on the blending effect of 5 wt% of PEMA in the polymer PVdF-HFP plasticized with plasticizer ethylene carbonate (EC), using acetone as the solvent. Two compositions of plasticized polymer electrolyte films, 50 wt % PVdF-HFP+ 35 wt % EC + 15 wt% $LiClO_4$ (**S1**), 45 wt % PVdF-

HFP + 5 wt % PEMA+ 35 wt % EC + 15 wt% $LiClO_4$ (**S2**) were prepared to study the effect of blending. The corresponding weight percentages of PVdF-HFP, PEMA, EC and $LiClO_4$ were dissolved in acetone and stirred well for 24 hrs. The obtained solution was then poured in a petri dish and evaporated at room temperature for about 48 hrs. Then obtained electrolyte film was further heated at 50 ^oC for 5 hrs in vacuum oven before subjecting to further studies. The electrolyte films S1 and S2 were explored using XRD (SHIMADZU-XRD-6000 diffractometer with Cu-Kα radiation, λ= 0.1541 nm as the source at 40 kV), FTIR (BRUKER-FTIR-ATR spectrometer) and AC impedance studies (CH-Instrument, CHI-600E) in the frequency range of 40 Hz to 1 MHz at room temperature, with an amplitude voltage of 50 mV.

Results and Discussion

The XRD pattern of the pure PVdF-HFP shows the presence of mixture of α and γ phases with the characteristic peaks at 2θ ~ 18°, 21°, 27°and 39°. This belongs to the planes (020), (110), (021) and (131) respectively of the crystalline part of PVdF-HFP (Figure 1.A). In case of film S1, the peaks corresponding to (020) and (021) planes were found fully suppressed, indicating an increase in amorphous nature of the film, due to the presence of plasticizer. Whereas, the film S2 blended with 5 wt % of PEMA (S2) shows an increase in broadness of the peaks when compared to film S1 (Figure 1.A). This shows further increase in amorphous nature of the film after blending with 5 wt % PEMA.

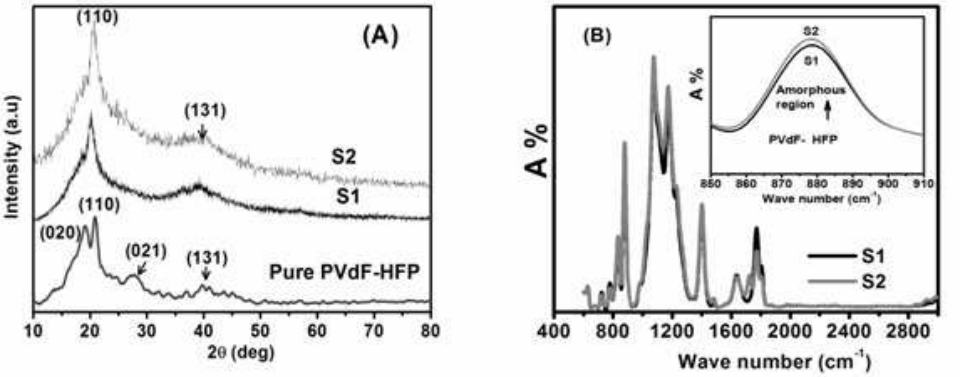

Figure.1 (A) XRD pattern and (B) FTIR spectra (inset: 850 to 910 cm^{-1}) of 50 wt % PVdF-HFP + 35 wt % EC + 15 wt% $LiClO_4$ (S1), 45 wt % PVdF-HFP + 5 wt % PEMA + 35 wt % EC + 15 wt% $LiClO_4$ (S2)

The FTIR spectra suggest the complete miscibility between the polymers (Figure.1.B). The characteristic bands of PVdF-HFP due to CH_2 wagging at 1397 cm^{-1}, bands at 2982 and 2911 cm^{-1} due to C-H stretching vibration, and bands at 1182 and 1065 cm^{-1} due to CF_2 groups were found in FTIR spectra of film S1 [3]. The bands at 624 $cm^{-1,}$ 1080 cm^{-1} and 941 cm^{-1} belongs to salt added. Similar spectra were obtained for film S2, with slight shift in band positions and changes in intensity. The band due to functional group of PEMA (carbonyl stretching (C=O)) was observed at 1722 cm^{-1} (film S2). The band at 877 cm^{-1} in films S1 and S2 was due to the amorphous region of PVdF-HFP (inset of Figure.1.B) [4]. The increase in area of amorphous region of PVdF-HFP at 876 cm^{-1} was found by calculating the area under the peak (after normalizing). It was found to be 15.98 in case of S1 and 17.13, in case of S2. This suggests an increase in amorphous nature of film S2.

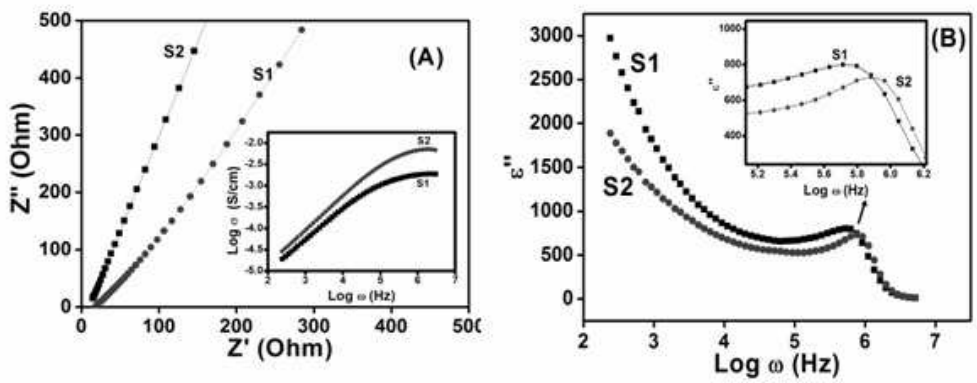

Figure.2 (A) Nyquist plot (inset: conductivity spectra) and (B) Dielectric Spectra of 50 wt % PVdF-HFP + 35 wt % EC + 15 wt% $LiClO_4$ (S1), 45 wt % PVdF-HFP + 5 wt % PEMA + 35 wt % EC + 15 wt% $LiClO_4$ (S2)

The Figure.2 (A) shows the Nyquist plot of S1 and S2 measured at room temperature. The presence of spike at the low frequency was due to the accumulation of lithium ions at the blocking electrodes. The resistances of the film were obtained by finding the intercept of the low frequency spike at the x-axis. The film S1 was found to have a conductivity value of 1.11×10^{-3} S/cm. The film S2 was found to have a conductivity value of 0.214×10^{-2} S/cm. This increase in conductivity was due to the increase in amorphous nature of the film S2 as discussed above in XRD and FTIR analysis. The conductance spectra for the film S1 and S2 at room temperature is shown in inset of fig. 2A. In both the cases, the extrapolating of mid frequency plateau region to the y-axis was found to give the dc conductivity value close to the values obtained from Nyquist plot. Figure.2 (B) shows the dielectric spectra of films S1 and S2. With addition of 5 wt % of PEMA, the β-relaxation was well pronounced and shifted to the high frequency region (inset fig. 2b) indicating a decrease in relaxation time (or increase in side chain movement) leading to increase in conductivity. The increased conductivity and the significant changes with respect to structural and vibrational nature of the film S2 signifies the need for a systematic study on the compositional effect of different wt % of PEMA, which is underway.

References

1. Ulaganathan M, Chitra M.Mathew, Rajendran S., Highly porous lithium-ion conducting solvent-free poly(vinylidenefluoride-co-hexafluoropropylene)/poly(ethyl methacrylate) based polymer blend electrolytes for Li battery applications, Electrochimica Acta., 2013, 93, 230– 235.
2. Rinaldo Crecorio, JR. and Marcelo cestari., Effect of Crystallization Temperature on the Crystalline Phase Content and Morphology of Poly (vinylidene Fluoride), J. Poly. Sci. Part B, Polymer Physics., 1994, 32, 859-870.
3. Sim L.N, Majid S.R, Arof A.K., FTIR studies of PEMA/PVdF-HFP blend polymer electrolyte system incorporated with LiCF3SO3 salt, Vibrational Spectroscopy., 2012, 58, 57-66.
4. Li Z, Su G, Gao D, Wang X, Li X., Effect of Al2O3 nanoparticles on the electrochemical characteristics of P(VDF-HFP)-based polymer electrolyte, Electrochimica Acta., 2004, 49, 4633– 4639.

*****