# Structural and ionic conductivity studies of electrospun polymer blend P(VdF-co-HFP)/PMMA electrolyte membrane for lithium battery application

O. Padmaraj, M. Venkateswarlu, and N. Satyanarayana

Citation: AIP Conference Proceedings **1665**, 060012 (2015); doi: 10.1063/1.4917847
View online: http://dx.doi.org/10.1063/1.4917847
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1665?ver=pdfcov
Published by the AIP Publishing

# Structural and Ionic Conductivity Studies of Electrospun Polymer Blend P(VdF-co-HFP)/PMMA Electrolyte Membrane for Lithium Battery Application

O.Padmaraj[1], M.Venkateswarlu[2] and N.Satyanarayana[1,*]

[1] *Department of Physics, Pondicherry University, Pondicherry 605 014, India*
[2] *R&D, Amara Raja Batteries Ltd., Karakambadi 517 520, India*
**E-mail: nallanis2011@gmail.com*

**Abstract.** A novel fibrous polymer blend [(100-*x*) % P(VdF-co-HFP)/*x* % PMMA, *x* = 10, 20, 30, 40, 50] electrolyte membranes were prepared by electrospinning technique. Structural, thermal and surface morphology of all the compositions of electrospun polymer blend membranes were studied by using XRD, DSC & SEM. The newly developed five different compositions of polymer blend fibrous electrolyte membranes were obtained by soaking in an electrolyte solution contains 1M $LiPF_6$ in EC: DEC (1:1,v/v). The wet-ability and conductivity of all the compositions of polymer blend electrolyte membranes are evaluated through electrolyte uptake and impedance measurements. The polymer blend [90% P(VdF-co-HFP)/10% PMMA] electrolyte membrane showed good wet-ability and high conductivity ($1.788 \times 10^{-3}$ $Scm^{-1}$) at room temperature.

**Keywords:** Electrospinning, Fibrous polymer blend electrolyte, Ionic conductivity.
**PACS:** 71.20 Rv, 72.80.Le, 72.80.Tm, 73.61.Ph

## INTRODUCTION

Lithium polymer batteries (LPBs) are continued to be a great demand, because of the superior electrochemical and physical properties of the polymer electrolyte (PE), as compared to liquid electrolyte used in conventional lithium batteries, such as flexibility in design, compactness, leak proof construction, safety, shelf life, energy density, etc [1-2]. Polyvinylidene fluoride (PVdF), poly(vinylidenefluoride-co-exafluoropropylene) P(VdF-co-HFP), polymethyl methacrylate (PMMA) and polyethylene oxide (PEO) have been widely used as host polymers for the preparation of PEs. Among them, P(VdF-co-HFP) has been found to be very promising polymer host matrix, as it has good electrochemical stability and high dielectric constant ($\varepsilon \approx 8.4$) [4]. But, the crystalline phase of P(VdF-co-HFP) hinders the migration of $Li^+$ ions and hence, batteries with P(VdF-co-HFP) based electrolyte membranes have lower charge/discharge capacities and poor C-rate values. Therefore, it is great importance to search for novel new PEs or modify the existing electrolyte materials to create new generation of high performance lithium batteries. Hence, in the present investigation, the authors are motivated to develop the blending of two polymers [(100-*x*) % P(VdF-co-HFP)/*x* % PMMA, *x* = 10, 20, 30, 40, 50] with various concentrations to reduce the crystalline phase with improved electrochemical properties for better performance of lithium polymer batteries.

## EXPERIMENTAL

### Synthesis of Polymer Blend Electrolyte

Poly(vinylidenedifluoride-co-hexafluoropropylene) P(VdF-co-HFP) and Polymethyl methacrylate (PMMA) were used as host polymers for the preparation of polymer blend electrolyte membranes by electrospinning method. Acetone and N, N-Dimethylacetamide (Ace: DMAc) (7:3, v/v) were used as mixed organic solvents. First, five different compositions [(100-*x*) % P(VdF-co-HFP)/*x* % PMMA, *x* = 10, 20, 30, 40, 50] of polymers were dissolved in the above mixed organic solvent under constant stirring for 6 h at room temperature. The resultant light viscous five different compositions of polymer blend solutions were taken into a 20 ml syringe and loaded in a syringe pump to develop polymer blend fibers by fixing the optimized electrospinning parameters such as solution feed rate 1.5 $mlh^{-1}$, applied

*Solid State Physics*
AIP Conf. Proc. 1665, 060012-1–060012-3; doi: 10.1063/1.4917847

voltage between spinneret and collector is 14 kV, distance between the tip of the spinneret and collector is 15 cm, needle bore size 24 G and collector drum rotation speed is 550 rpm. The electrospun polymer blend multi-fibrous layered membranes with an average thickness of 80 $\mu$m were collected on the rotating drum collector and further it was dried in hot air oven at 60 °C for 24 h to remove the solvent.

## Characterization

All the prepared samples were characterized by XRD using PANalytical X-pert PRO diffractometer (Philips), DSC curves were recorded on DSC $Q_{20}$ instrument under nitrogen atmosphere and scanning electron microscopy (SEM, Hitachi S4700). The electrolyte uptake was calculated based on the following equation.

$$\mathbf{EU = W_1\text{-}W_2/W_0 \times 100\ \%} \qquad (1)$$

where, $W_1$ and $W_0$ are the weights ($gm$) of the wet and dry membranes respectively. The conductivity of all the prepared fibrous PMMA blend electrolyte membranes was calculated by analyzing measured impedance spectra using Frequency response analyzer (Novocontrol). Each of the prepared electrolyte membrane was placed between two stainless steel electrodes and measured the impedance data in the frequency range from 1 MHz to 1 mHz at room temperature. The conductivities ($\sigma$) of all the prepared electrolyte membranes were calculated using the following equation

$$\boldsymbol{\sigma = t\ /AR_b} \qquad (2)$$

where, $t$ is the thickness, $A$ is the area and $R_b$ is the bulk resistance of the fibrous membranes.

## RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of P(VdF-HFP) copolymer and different compositions of polymer blend [(100-$x$)% P(VdF-co-HFP)/$x$% PMMA, $x$ = 10, 20, 30, 40, 50] membranes. From fig. 1, the observed diffraction pattern of pure copolymer showed a broad low intensity diffraction peak at 20°, which correspond to the PVdF crystallization phase [3]. The observed PVdF crystalline phase peak intensity decreased drastically and disappeared in the polymer blend fibrous membranes with the addition of various amounts of PMMA [($x$ %) PMMA, $x$ = 10, 20, 30, 40 & 50 %] content. This reveals that the crystallinity of PVdF decreased with the addition of PMMA, which in turn may enhance the conductivity at room temperature.

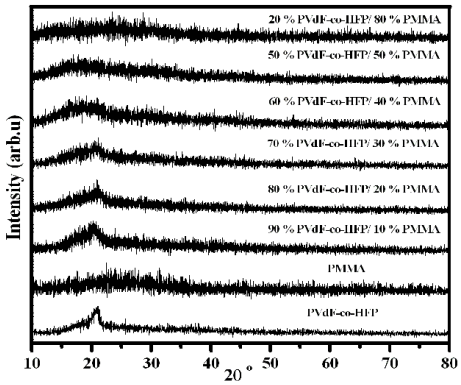


**FIGURE 1.** XRD patterns of pure and PMMA blend membranes.

Figure 2 shows the DSC curves of each composition of polymer blend [(100-$x$)% P(VdF-co-HFP)/$x$ % PMMA, $x$ = 10, 20, 30, 40, 50] membranes. From fig.2, the each curve exhibits two endothermic peaks at ≈ 75°C & 145 °C corresponding to the melting temperatures ($T_m$) of PMMA & P(VdF-co-HFP) respectively. This indicates that homogeneous blending of P(VdF-co-HFP) and PMMA has been accomplished as a result of the possible chemical-oriented co-ordination between the 'mer' units of two polymers, which assures the better blending [3].

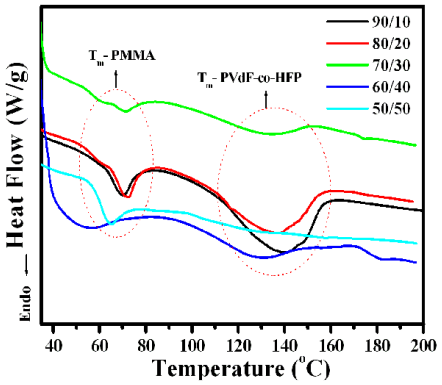


**FIGURE 2.** DSC curves of polymer blend membranes.

Figure 3 shows the SEM images of electrospun P(VdF-co-HFP) (fig.3a) and polymer blend fibrous membranes [(100-$x$)% P(VdF-co-HFP)/$x$ % P(MMA)] with various PMMA [10% (fig.3b), 20% (fig.3c), 30% (fig.3d), 40% (fig.3e) & 50% (fig.3f)] content. In fig.3, all the SEM images showed three dimensional web-like structures with fully interconnected ultrafine multi-fiber layers. The interlaying of multi-fiber layers generates a nano/micro porous structure between the ultrafine fibers, which may be able to absorb and retain the electrolyte effectively [4].

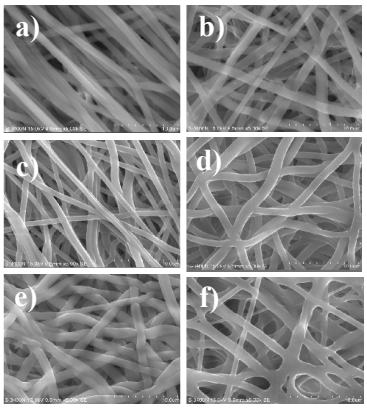


**FIGURE 3.** SEM images of polymer blend [(100-*x*) % P(VdF-co-HFP)/*x*% PMMA, *x* = 0,10, 20, 30, 40, 50] membranes.

Figure 4 shows the variation of electrolyte uptake and conductivity of polymer blend electrolyte membranes with various PMMA content. In fig.4, the electrolyte membrane with 10% of PMMA content exhibits 60% of increment in electrolyte uptake and further addition of PMMA content (20%, 30%, 40% & 50%) results in decrease from 60% to 40%. The increment in electrolyte uptake is mainly due to the affinity of PMMA with carbonate based electrolyte, which may lead to enhance the conductivity of polymer blend fibrous electrolyte membranes.

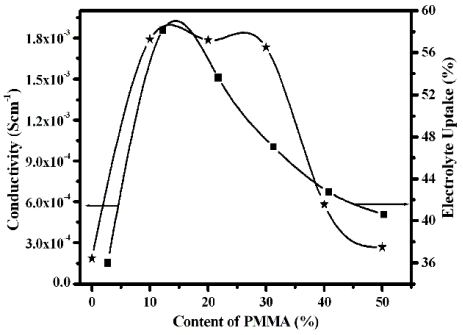


**FIGURE 4.** Variation of electrolyte uptake & conductivity with various PMMA content.

Figure 5 shows the complex impedance spectra of polymer blend [(100-*x*)% P(VdF-co-HFP)/*x*% PMMA, *x* = 10, 20, 30, 40, 50] electrolyte membranes at room temperature. In fig.5, each impedance spectra show one arc and an inclined spike in the measured frequency range. The intercept of inclined spike on the real axis gives the bulk resistance ($R_b$) [4]. The observed impedance spectra were fitted using "Win FIT" software and obtained its bulk resistance in the form of equivalent circuit. The conductivity (σ) of each polymer blend electrolyte membrane was calculated from the analyzed impedance data and sample dimensions. The calculated conductivities are found to be $1.875 \times 10^{-4}$ S/cm (0%), $1.788 \times 10^{-3}$ S/cm (90/10), $1.773 \times 10^{-3}$ S/cm (80/20), $1.730 \times 10^{-3}$ S/cm (70/30), $5.799 \times 10^{-3}$ S/cm (60/40) & $2.675 \times 10^{-3}$ S/cm (50/50). The variation of conductivity with PMMA content is shown in fig. 4. The increase of conductivity by blending 10% PMMA is due to the increase of liquid electrolyte uptake and also the formation of the amorphous phase, which may contributes to the formation of more tunnels allowing greater Li ion migration compare to other compositions.

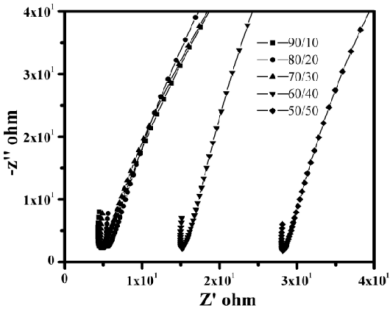


**FIGURE 5.** Complex impedance spectra of polymer blend [(100-*x*) % P(VdF-co-HFP)/*x* % PMMA, *x* =10, 20, 30, 40, 50] electrolyte membranes.

## CONCLUSION

The electrospun polymer blend [(100-*x*)% P(VdF-co-HFP)/*x* % PMMA, *x* = 10, 20, 30, 40 & 50] fibrous electrolyte membranes were prepared by electrospinning technique. The fibrous polymer blend [90% P(VdF-co-HFP)/10% PMMA] membrane showed the reduction of PVdF crystallinity, high thermal stability, high electrolyte uptake, high ionic conductivity at room temperature. Hence, the newly developed electrospun polymer blend [90% P(VdF-co-HFP)/10% PMMA] electrolyte membrane can be used as a separator-cum electrolyte membrane for rechargeable lithium polymer batteries.

## ACKNOWLEDGEMENT

Dr. NS is gratefully acknowledges DST, AICTE, UGC, CSIR and DRDO, Govt. of India for financial support through major research project grants.

## REFERENCES

1. Y Wang, D Kim, *Electrochim Acta* **52**, 3181-3189 (2007).
2. A M Stephen, K S Nahm, *Polymer* 47, 5952-5964 (2006).
3. Y Liang, S Cheng, J Zhao, C Zhang, S Sun, N Zhou, Y Qiu, X Zhang, *J. Power sources* 240, 204-211 (2013).
4. X Li, G Cheruvelly, J K Kim, J W Choi, J H Ahn, K W Kim, H J Ahn, *J. Power sources* 167, 491-498 (2007).