

Synthesis, characterization and electrochemical performance of electrospun nanocomposite polymer blend [P(VdF-co-HFP)/PMMA/ZnAl₂O₄] electrolyte fibrous membrane for lithium battery

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ABSTRACT

Hybrid electrospun nanocomposite polymer blend electrolyte (NCPBE) fibrous membranes with an incorporation of various x wt.% of ZnAl₂O₄, ($x = 2, 4, 6$ and 8) ceramic fillers were prepared by an electrospinning technique. All the prepared electrospun pure and NCPBE fibrous membranes were characterized using X-ray diffraction, fourier transform infrared spectroscopy, differential scanning calorimetry and scanning electron microscopy. Among the prepared, NCPBE fibrous membrane with 6 wt.% ZnAl₂O₄ ceramic filler showed low crystallinity, high thermal stability, low average fiber diameter, high electrolyte uptake and high conductivity ($4.13 \times 10^{-3} \text{ Scm}^{-1}$) at room temperature. Further, the optimized best conducting composition of NCPBE membrane with 6 wt.% ZnAl₂O₄ fillers content is used for the fabrication of CR 2032 coin type lithium cell (Li/NCPBE/LiCoO₂). The newly fabricated coin type lithium polymer cell delivers an initial discharge capacity of 157 mAh g⁻¹ and also exhibits stable cycle performance at current density of 0.1 C - rate at room temperature.

Keywords: Polymer blend, ZnAl₂O₄, Electrospinning, Impedance, Charge/discharge.

1 INTRODUCTION

Recent years, lithium-ion batteries (LIBs) have been used as a best power sources for portable, household electronic devices, aerospace, hybrid electric vehicles (HEVs), etc. [1]. Most of the available commercial lithium-ion batteries face some safety issues such as high vapor pressure, low flash point, dendrite growth formation and leakage [2]. In order to overcome the aforementioned issues, researchers have been focussing to develop solid polymer electrolyte (SPE) as a better alternative. SPEs are having unique properties, including: a simple design with desired size and shape, leak proof construction, wider electrochemical stability, better safety, etc [3]. But, SPEs have low ionic conductivity ($\sim 10^{-8} \text{ Scm}^{-1}$) at room temperature as compared to organic liquid electrolytes. In order to improve the ionic conductivity at room temperature, many efforts have been made to develop high conducting PEs by adding plasticizer, polymer blend and

ceramic fillers [4-6]. For PEs, poly(vinylidene fluoride) (PVdF), poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP), poly (methyl methacrylate) (PMMA), poly(ethylene oxide) (PEO) and poly(styrene) (PS) have been widely used as host polymers [7-11]. Among them, P(VdF-co-HFP) copolymer is found to be a suitable promising material, because of its good electrochemical stability, affinity to electrolyte solution and high dielectric constant ($\epsilon \approx 8.4$). But, the crystalline part of PVdF in P(VdF-co-HFP) copolymer hinders the migration of Li⁺ ions [10]. Hence, the P(VdF-co-HFP) based membranes can be modified by blending of PMMA polymer and addition of nanosized ZnAl₂O₄ ceramic fillers. Various methods such as solution casting, plasticizer extraction, phase inversion, electrospinning, etc., have been reported. Among them, electrospinning is a simple and effective technique to develop micro size porous polymer fibrous membranes with highly interconnected porous structure with large surface area [10, 11].

Hence, authors are motivated to develop the electrospun NCPBE membranes with an incorporation of 10% PMMA blend and nanocrystalline x wt.% ZnAl₂O₄, ($x = 2, 4, 6$ & 8 wt%) ceramic particles as fillers. Pure SPE and NCPB fibrous membranes were characterized using XRD, FTIR, DSC and SEM techniques to find their structural, thermal and physical properties respectively. The NCPBE membranes were activated by immersing the prepared fibrous membranes in a carbonate based electrolyte solution [1M LiPF₆ in EC:DEC (1:1, v/v)]. The ionic conductivities of an activated NCPBE membranes were evaluated through impedance measurements at room temperature. Further, CR2032 coin type lithium polymer cells [Li/NCPBE/LiCoO₂] were assembled inside an argon filled glove box and studied their electrochemical performance using battery cycle tester (BCT) at current density of 0.1 C-rate.

2 EXPERIMENTAL

2.1 Synthesis of electrospun NCPBE fibrous membranes

Poly(vinylidene difluoride-co- hexafluoropropylene) [P(VdF-co-HFP)], Poly(methyl methacrylate) [PMMA] were used as host polymer and ZnAl_2O_4 nanocrystalline particles were used as ceramic fillers for the preparation of NCPB fibrous membranes by an electrospinning method. Acetone and N, N-Dimethylacetamide (Ace:DMAc) (7:3, v/v) were mixed and used as solvent. First, an optimized 16 wt.% P(VdF-co-HFP)/PMMA (90/10) was dissolved separately in a mixed solvent under continuous stirring for 5 h at room temperature. Later, various amounts of nanocrystalline x wt.% ZnAl_2O_4 , ($x = 2, 4, 6$ and 8) nanoparticles were dispersed in a mixed solvent separately under ultrasonication. Then, the dispersed ceramic particles were slowly added into the optimized polymer blend solution under constant stirring. The resultant light viscous polymer blend solution was taken into a 20 ml syringe for electrospinning. The following electrospinning parameters are fixed for all the compositions: solution feed rate 1.5 ml h^{-1} , applied voltage between spinneret and collector is 16 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 collected multi-fibrous membranes with an average thickness of $80 \mu\text{m}$ was dried in hot air oven at 60°C for 24 h to remove the solvent for further use. The pure and NCPBE membranes were prepared by soaking into a liquid electrolyte of 1M LiPF_6 in EC: DEC (1:1, v/v) for 30 min in a dry glove box.

2.2 Characterization techniques

X-ray diffraction (XRD) patterns were recorded from 10° to 80° for all the prepared electrospun membranes using Panalytical X-pert pro diffractometer (Philips) with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154060 \text{ nm}$, 30 mA and 40 kV). The surface morphology of all the electrospun membranes was investigated, using scanning electron microscopy (SEM, Hitachi S4700). The electrical behavior of each composition of NCPBE membrane was evaluated through impedance spectroscopy. The prepared each NCPBE membrane was placed between two blocking stainless steel (ss) electrodes and measured the impedance in the frequency range of 1 mHz - 1 MHz. The conductivity of each membrane was calculated using sample dimensions and bulk resistance.

The CR 2032 coin type lithium cells were fabricated inside an Argon-filled glove box [Vacuum Atmospheres Co. (VAC), USA] by sandwiching the prepared NCPBE membrane between lithium metal anode ($380 \mu\text{m}$ thick, Aldrich) and composite LiCoO_2 cathode. The composite cathode slurry was prepared by mixing 70 wt% of active material (LiCoO_2), 20 wt% of conducting super P carbon and 10 wt% of PVdF binder (Aldrich) in N-methyl pyrrolidinone (NMP) solvent. The resulting slurry was coated onto an Al-foil ($\sim 20 \mu\text{m}$ thick) using doctor blade method and dried in hot air vacuum oven at 120°C for 24 h. The charge/discharge cycles tests of the assembled coin cells [$\text{Li}/\text{NCPBE}/\text{LiCoO}_2$] were performed at room

temperature using battery cycle tester (BCT) (Model MCV4-1/0.01/0.001-10, Bitrode, USA) between the potentials 2.8-4.2 V at a current density of 0.1 C-rate.

3 RESULTS AND DISCUSSION

X-ray diffraction (XRD) patterns of the electrospun pure and NCPB fibrous membranes along with the prepared ZnAl_2O_4 ceramic nanofillers are shown in fig.1. From fig.1, the observed diffraction pattern of pure P(VdF-co-HFP) copolymer membrane showed one low intensity broad diffraction peak at $2\theta = 20.1^\circ$, which is compared with the standards JCPDS data (Card No.00-038-1638) and confirmed the presence of PVdF crystalline phase in P(VdF-co-HFP) copolymer [31-33]. The intensity of diffraction peak of PVdF is decreased drastically by an addition of 10% PMMA content as shown in fig. 1, which confirms the reduction of PVdF crystallinity. Further, the intensity of the diffraction peak of the electrospun NCPB fibrous membrane is decreased by the addition of various amounts of x wt.% of ZnAl_2O_4 , ($x=2, 4, 6$ and 8) ceramic fillers upto 6 wt.%. This indicates the formation of amorphous nature, due to the Lewis acid-base interactions between polymer blend matrix and ceramic fillers [8]. The amorphous nature of the NCPB fibrous membrane can provide more conducting pathways, which may help to increase the mobility (μ) of ions and hence, improves the conductivity. Further, addition of 8 wt.% ZnAl_2O_4 fillers content, the intensity of diffraction peaks of NCPB fibrous membrane increase, which indicate the formation of ZnAl_2O_4 crystalline phase is increased. This may affect the mobility (μ) of free Li-ion charge carriers by blocking or hindering the path ways, which may decrease the conductivity and further, it was confirmed from the conductivity results.

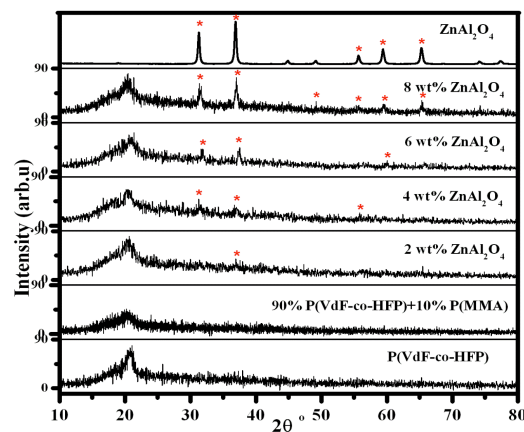


Figure 1 X-ray diffraction patterns of electrospun pure P(VdF-co-HFP), polymer blend and nanocomposite polymer blend fibrous membranes with an addition of x wt% ZnAl_2O_4 , ($x = 2, 4, 6$ and 8) ceramic fillers.

Figure 2 shows the SEM images of electrospun P(VdF-co-HFP), P(VdF-co-HFP)/PMMA (90/10) blend and

nanocomposite polymer blend fibrous membranes with an addition of various content of x wt.% ZnAl_2O_4 , ($x = 2, 4, 6$ and 8) ceramic fillers. From fig.2, all the SEM images showed three dimensional web-like structures with fully interconnected ultrafine multi-fiber layers. The interlaying of multi-fiber layers generate a nano/micro porous structure, which may be able to absorb/retain electrolyte effectively [9]. From the observed SEM images, the average fiber diameter (AFD) of all the electrospun membranes were measured. Among them, the NCPB fibrous membrane with 6 wt.% of ZnAl_2O_4 fillers content exhibits less AFD (250 nm) with uniform fiber distribution compared to other compositions of composites.

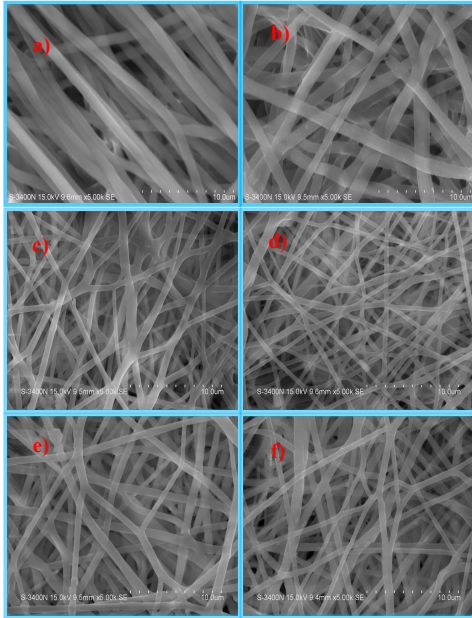


Figure 2 SEM images of electrospun a) pure P(VdF-co-HFP), b) polymer blend [90% P(VdF-co-HFP)/10% PMMA] and NCPB fibrous membranes with x wt.% ZnAl_2O_4 (c) 2, (d) 4, (e) 6 and (f) 8.

All the prepared electrospun P(VdF-co-HFP)/PMMA (90/10) blend and nanocomposite polymer blend fibrous membranes with various contents of x wt.% ZnAl_2O_4 , ($x = 2, 4, 6$ and 8) fillers were activated into separator-cum polymer electrolyte by soaking in an electrolyte solution, containing of 1M LiPF_6 in EC: DEC (1:1, v/v). The moment that the drop of liquid electrolyte is poured on the developed electrospun membranes, it spreads quickly on the surface and penetrates into the membrane within a second. This implies that the developed electrospun fibrous membranes having good porous structure and also having good electron affinity between the polymer matrixes and liquid electrolyte, which may help quick absorption/penetration of liquid electrolyte into the fibrous membranes.

Figure 3 shows the complex impedance spectra of electrospun polymer blend and NCPBE fibrous membranes

with various contents of x wt.% of ZnAl_2O_4 , ($x = 2, 4, 6$ and 8) ceramic fillers at room temperature. In fig. 3, the impedance spectrum of each electrolyte membrane show one arc and an inclined spike in the measured frequency range. The intercept of an inclined spike on the real axis (Z') represents the bulk resistance (R_b) of each composition of NCPBE membrane [9]. The observed impedance responses were fitted using “WinFIT” software to evaluate the electrical response of each fibrous electrolyte membrane in the form of an equivalent circuit. The electrical conductivity (σ) of each composition of NCPBE membranes were calculated using the evaluated bulk resistance (R_b), sample dimensions [area (A) and thickness (t)]. The calculated highest conductivity of NCPBE membrane with 6 wt.% of ZnAl_2O_4 fillers content is found to be $4.135 \times 10^{-3} \text{ Scm}^{-1}$ at room temperature.

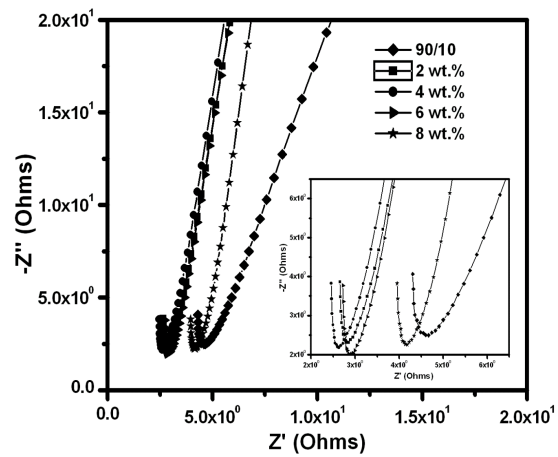


Figure 3 Complex impedance spectra of electrospun polymer blend (90/10) and NCPBE membranes with various contents of x wt.% ZnAl_2O_4 , ($x = 2, 4, 6$ and 8) ceramic fillers at room temperature.

The variation of electrical conductivity and electrolyte uptake with respect to the addition of various contents of x wt.% ZnAl_2O_4 , ($x = 2, 4, 6$ and 8) ceramic fillers are shown in fig. 4. In fig. 4, the electrical conductivity increases with an addition of ZnAl_2O_4 ceramic fillers content up to 6 wt.%, which may be due to the formation of more conduction pathways in the amorphous phase, showing improved Li-ion migration with electrolyte absorption. Further, addition of 8 wt.% of ZnAl_2O_4 ceramic fillers content results in decrease of electrical conductivity, which may be due to the formation of agglomerated ZnAl_2O_4 particles. The agglomerated ZnAl_2O_4 particles may lead to block or hinder the migration of Li-ions in the NCPBE membranes. Hence, the optimized NCPBE membrane with 6 wt.% of ZnAl_2O_4 fillers content can be swollen sufficiently with the organic liquid electrolyte, which may lead to increase the ionic conductivity at room temperature.

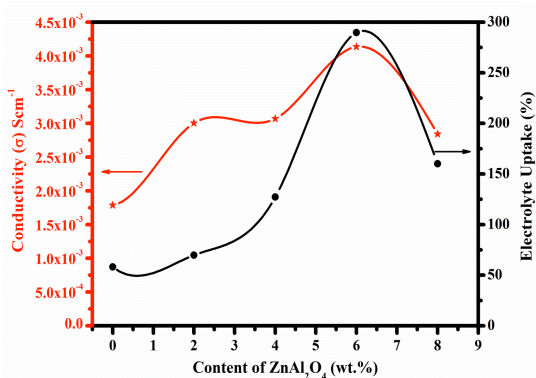


Figure 4 Variation of electrical conductivity (red colour line) of electrospun polymer blend and NCPBE fibrous membranes with respect to x wt% ZnAl_2O_4 , ($x = 2, 4, 6$ and 8) ceramic filler contents at room temperature.

Figure 5 shows a comparative charge-discharge curves of CR 2032 lithium cells containing the optimized NCPBE fibrous membrane with 6 wt.% of ZnAl_2O_4 fillers content at a current density of 0.1 C-rate. From fig. 5, the discharge capacity of NCPBE fibrous membrane is found to be 157 mAh g^{-1} for 1st cycle and 132 mAh g^{-1} for 30th cycle. The observed capacity, difference from 1st to 30th cycles, of assembled coin type lithium cell showed an approximately 25 mAh g^{-1} , which is probably due to the difference in Li-ion conductivity and utilization of active material [10,11]. The optimized NCPBE membrane has high porosity with ultra-fine pore structure, which might have absorbed large amount of liquid electrolyte. This may help to enhance the ionic conductivity by entrap the Li ions into the electrolyte fibrous membrane, which indicate the higher utilization of active material by sustains the absorbed electrolyte through charge/discharge process.

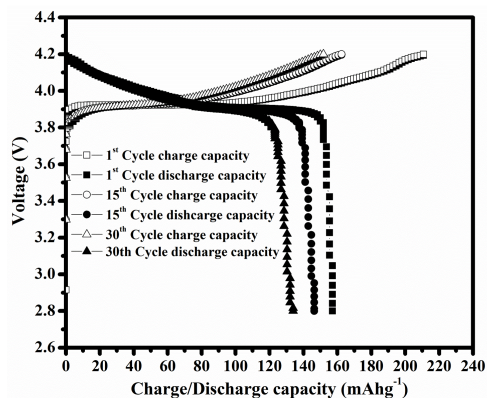


Figure 5 Charge-discharge capacity of CR 2032 coin type lithium cell containing the NCPBE fibrous membrane with 6 wt.% of ZnAl_2O_4 fillers content at room temperature.

4 CONCLUSION

The as-prepared electrospun nanocomposite polymer blend (NCPBE) fibrous membranes with various contents of

ZnAl_2O_4 ceramic fillers were prepared by an electrospinning technique. The NCPBE fibrous membrane with 6 wt.% of ZnAl_2O_4 fillers content showed the reduction of PVDF crystallinity and low average fiber diameter with uniform morphology. The activated nanocomposite polymer blend electrolyte (NCPBE) fibrous membranes [90% P(VdF-co-HFP)/10% PMMA /6 wt.% ZnAl_2O_4 /1M LiPF_6] showed high ionic conductivity with good electrochemical stability at room temperature. The fabricated CR 2032 coin type lithium cell containing the high conductivity composition of NCPBE fibrous membranes with 6 wt.% of ZnAl_2O_4 fillers content delivers the good charge-discharge capacity at room temperature. Hence, the newly developed electrospun nanocomposite polymer blend electrolyte fibrous membrane can be used as a separator-cum polymer electrolyte membrane for high performance rechargeable lithium batteries as well as other electrochemical device applications.

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REFERENCES

- [1] L. Su, Y. Jing, Z. Zhou, *Nanoscale*, 3, 3967-3983, 2011.
- [2] C.W. Walker Jr., J.D. Cox, M. Salomon, *J. Electrochem. Soc.*, 143, L80-L82, 1996.
- [3] J. Xi, X. Qiu, J. Li, X. Tang, W. Zhu, L. Chen, *J. Power Sources*, 157, 501, 2006.
- [4] M. Stephen, *Eur. Pol. J.*, 42, 21-42, 2006.
- [5] A. Sarnowska, I. Polska, L. Niedzicki, M. Marcinek, A. Zalewska, *Electrochim. Acta*, 57, 180-186, 2011.
- [6] F. Croce, G. B. Appetecchi, L. Persi, B. Scrosati, *Nature*, 394, 456-458, 1998.
- [7] J.Y. Song, Y.Y. Wang, C.C. Wan, *J. Power Sources*, 77, 183-197, 1999.
- [8] S. Rajendiran, R. Kannan, O. Mahendran, *J. Power Sources*, 96, 406-410, 2001.
- [9] A. Subramania, N.T. Kalyana Sundaram, A.R. Sathiya Priya, G. Vijaya Kumar, *J. Memb. Sci.*, 294, 8-15, 2007.
- [10] O. Padmaraj, B. Nageswara Rao, M. Venkateswarlu, N. Satyanarayana, *J. Phys. Chem. B*, 119, 5299-5308, 2015.
- [11] O. Padmaraj, M. Venkateswarlu, N. Satyanarayana, *Electroanalysis*, 26, 1-8, 2014.