



# Poly(methyl methacrylate) reinforced poly(vinylidene fluoride) composites electrospun nanofibrous polymer electrolytes as potential separator for lithium ion batteries

Yogita P. Mahant<sup>1</sup> · Subhash B. Kondawar<sup>1</sup> · Deoram V. Nandanwar<sup>2</sup> · Pankaj Koinkar<sup>3</sup>

Received: 12 January 2018 / Accepted: 21 March 2018 / Published online: 27 March 2018  
© The Author(s) 2018

## Abstract

Fabrication of nanofibrous polymer electrolyte membranes of poly(vinylidene fluoride) (PVdF) and poly(methyl methacrylate) (PMMA) in different proportion (PVdF:PMMA = 100:0, 80:20 and 50:50) by electrospinning is reported to investigate the influence of PMMA on lithium ion battery performance of PVdF membrane as separator. As-fabricated polymer electrospun nanofibrous membranes were characterized by SEM, FTIR, XRD, TGA and DSC for morphology, structure, crystallinity and thermal stability. PVdF–PMMA (50:50) polymer electrolyte membrane showed ionic conductivity 0.15 S/cm and electrolyte uptake 290% at room temperature. After 50 cycles, the discharge capacity 140 mAh/g of Li/PE/LiFePO<sub>4</sub> cells with PVdF–PMMA (50:50) as polymer electrolyte (PE) membrane was found to be retained around 93.3%. The electrolyte uptake, ionic conductivity, and discharge capacity retention were improved by optimizing the proportion of PMMA in PVdF. Nanofibrous PVdF–PMMA (50:50) polymer electrolyte membrane was found to be a potential separator for lithium ion batteries.

**Keywords** Poly(vinylidene fluoride) · Poly(methyl methacrylate) · Polymer electrolyte · Electrospinning · Nanofibers · Lithium ion batteries

## Introduction

Lithium ion batteries have been improved using polymer nanofibrous electrolyte membrane with its highly porous structure, high electrolyte uptake and ionic conductivity to transport as much as lithium ions through it. Polymer nanofibrous electrolyte membrane provides wide electrochemical operating window and good thermal stability useful to prevent electrolyte leakage and to minimize the firing hazard for high safety of batteries as compared to liquid

polymer electrolyte [1–6]. Poly(ethylene oxide) (PEO), polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVDF), poly(vinyl alcohol) (PVA) and poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF–HFP) have been studied as host polymer for fabricating nanofibrous polymer electrolyte membrane [7–16]. Among these polymers, poly(vinylidene fluoride) (PVdF) has been mostly used as a semi-crystalline polymer with excellent film-forming ability, high dielectric constant and thermal stability [17]. But the crystalline domains of PVdF restrict the penetration of liquid electrolytes and the movement of lithium ions from between the electrodes during charging and discharging which show low ionic conductivity. Therefore, researchers in this field are more engaged to prepare polymer electrolyte membranes by blending or forming composites using different polymers or metal oxides to increase ionic conductivity, electrolyte uptake, and electrochemical stability than that of pure polymer electrolytes [18–22]. Li et al. prepared PVDF/PMMA membrane by anchoring PMMA to multiporous PVDF surface via electron beam preirradiation grafting technique and showed ionic conductivity  $6.1 \times 10^{-3}$  S/cm [23]. Also, Idris et al.

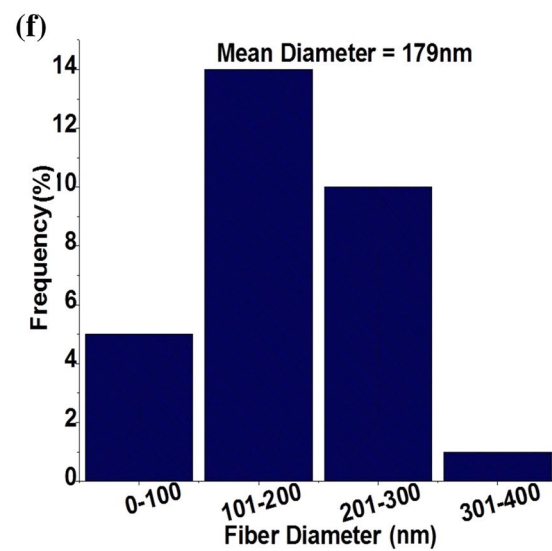
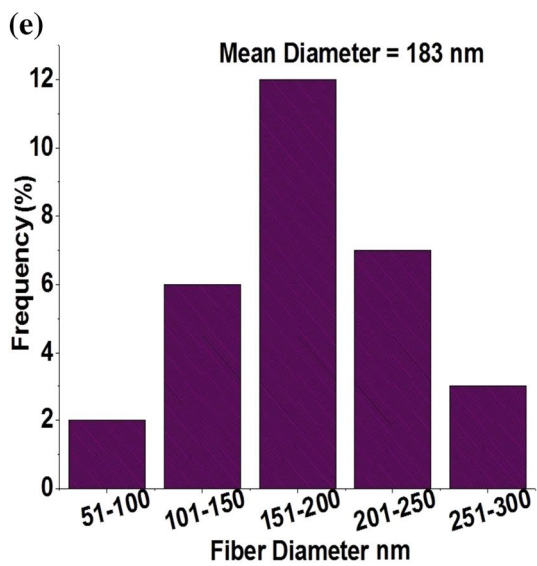
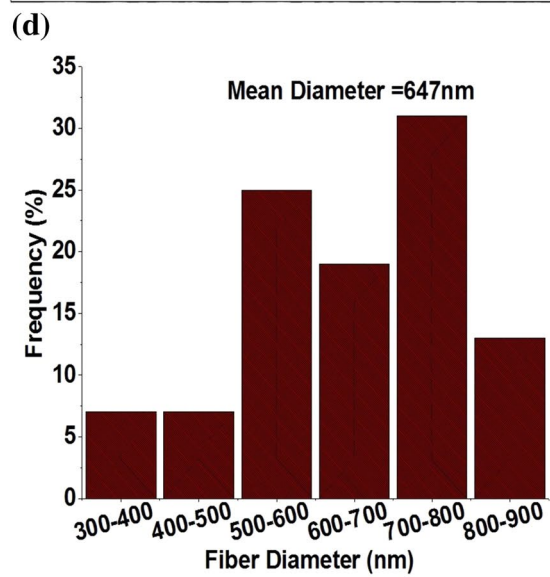
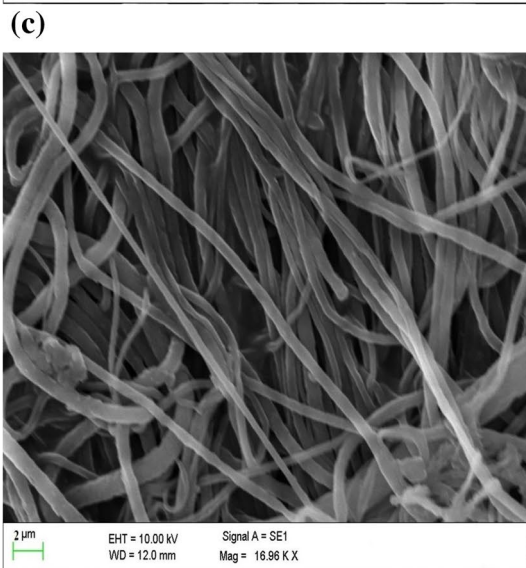
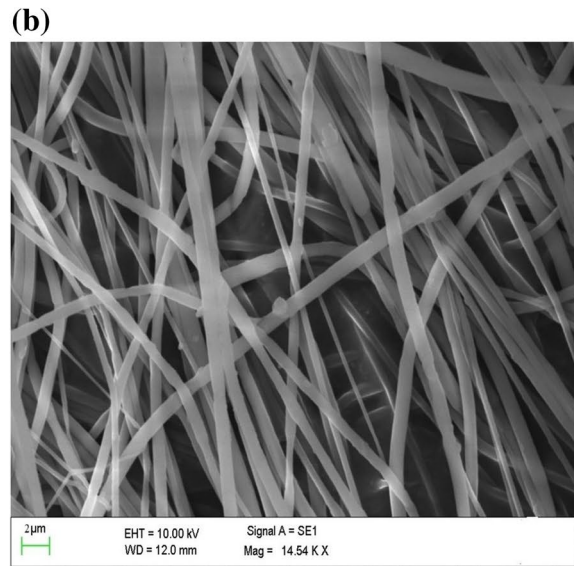
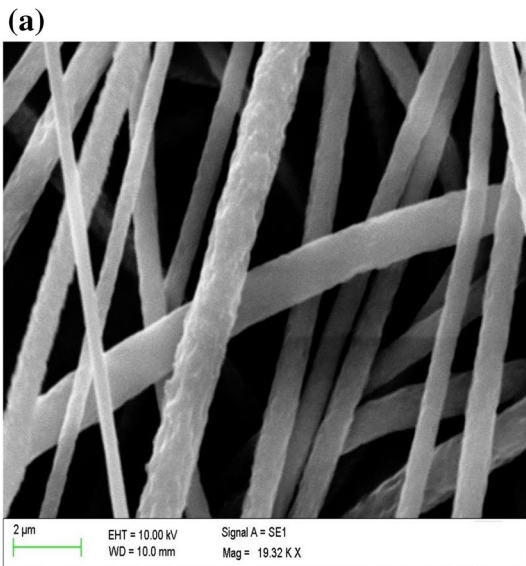
✉ Subhash B. Kondawar  
sbkondawar@yahoo.co.in

✉ Pankaj Koinkar  
koinkar@tokushima-u.ac.jp

<sup>1</sup> Department of Physics, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur 440033, India

<sup>2</sup> Department of Physics, Shri Mathuradas Mohata College of Science, Nagpur 440023, India

<sup>3</sup> Department of Optical Science, Tokushima University, Tokushima 7708506, Japan



**Fig. 1** **a** SEM image of electrospun PVdF nanofibrous membrane. **b** SEM image of electrospun PVdF–PMMA (80:20) nanofibrous membrane. **c** SEM image of electrospun PVdF–PMMA (50:50) nanofibrous membrane. **d** Histogram of electrospun PVdF nanofibrous membrane. **e** Histogram of electrospun PVdF–PMMA (80:20) nanofibrous membrane. **f** Histogram of electrospun PVdF–PMMA (50:50) nanofibrous membrane

prepared PVdF/PMMA microporous membranes using the phase-separation method with increasing percentage of PMMA and showed discharge capacity of 133 mAh/g [24]. Many different synthesis methods are used to prepare polymer electrolyte membrane by solution casting [15, 20], phase inversion [25] and electrospinning [26]. Among them, electrospinning is a simple method for preparation of nanofibrous membranes with high porosity due to tunable fiber diameter controlled by varying applied electric field, distance between syringe needle and grounded collector, polymer solution concentration, and flow rate of viscous polymer solution. Porosity is the size-dependent property; therefore, electrospun nanofibers of blended polymers synthesized by electrospinning possess high porosity which is responsible for increase in electrolyte uptake and high ionic conductivity at room temperature [27, 28]. Li et al. and Mahant et al. prepared fibrous membranes of poly(vinylidene fluoride)/poly(methyl methacrylate) (PVdF/PMMA) by electrospinning method and showed ionic conductivity  $3.5 \times 10^{-3}$  and  $2.95 \times 10^{-3}$  S/cm, respectively [29, 30]. Therefore, efforts have been made to optimize the composition of PVdF and PMMA to fabricate their composites nanofibrous membrane by electrospinning so as to increase the ionic conductivity.

In this work, the fabrication of polymer nanofibrous electrolyte membranes of PVdF–PMMA composites in different proportion (PVdF:PMMA = 100:0, 80:20 and 50:50) by electrospinning is reported to investigate the influence of PMMA on lithium ion battery performance. The effect of concentration of PMMA in composites on morphology, ionic conductivity, porosity and discharge capacity retention for lithium ion battery separator is studied and systematically compared.

## Experimental

### Preparation of PVdF–PMMA composites nanofibrous polymer electrolytes

PVdF–PMMA composites were prepared with varying weight ratio of PMMA in PVdF. The total polymer concentration was fixed at 15 wt%. PVdF–PMMA composites nanofibrous membranes in different proportion of PVdF and PMMA were prepared by electrospinning. In a typical procedure for the preparation of PVdF–PMMA (50:50) nanofibrous membrane, 15% PVdF–PMMA (5:5, w/w)

was dissolved in a mixed solvent *N,N*-dimethylformamide (DMF)/tetrahydrofuran (THF) (7:3, V/V) and magnetically stirred to form a homogeneous solution and then transferred the mixed polymer solution to disposable syringe for electrospinning to get continuous nanofibers. During electrospinning, computer controlled flow rate 0.6 ml/h, electric field 20 kV and distance 18 cm between the syringe needle and grounded collector (aluminum foil) were maintained. The nanofibrous membrane on the collector plate was dried under vacuum at 70 °C for 12 h and then separated from the foil for preparation of polymer electrolyte. In the similar way, PVdF–PMMA (50:50) and PVdF–PMMA (100:00) abbreviated as pure PVdF have been prepared by electrospinning with the same operating conditions. PVdF–PMMA nanofibrous polymer electrolytes were prepared by immersing the electrospun nanofibrous membranes in 1 M LiPF<sub>6</sub> (lithium hexafluorophosphate) in EC:DMC (1:1 v/v) (ethylene carbonate and dimethyl carbonate) solution at room temperature in a glove box under nitrogen atmosphere.

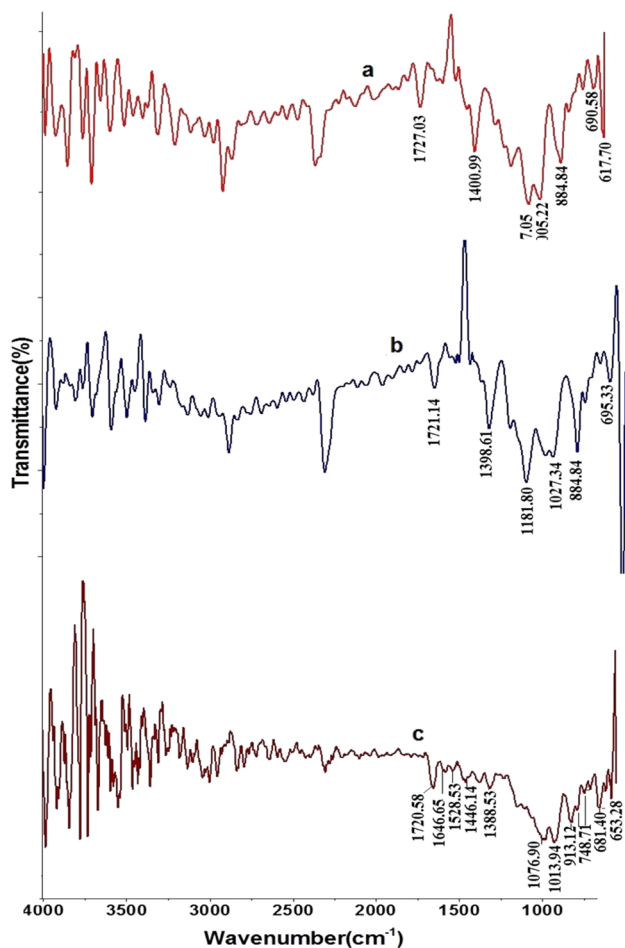
## Characterizations

The surface morphology of electrospun nanofibrous membranes was investigated by scanning electron microscope (CARL ZEISS EVO-18). Fourier transform infrared (FTIR) spectra of electrospun nanofibrous membranes were obtained on  $\alpha$ -Bruker model. X-ray diffraction (XRD) patterns of electrospun nanofibrous membranes were on Rigaku Miniflex II Desktop X-ray diffractometer. The crystallinity of electrospun nanofibrous membranes was obtained using differential scanning calorimetry (DSC) (Mettler Toleno DSC 822 e) with heating rate 10 °C per min under N<sub>2</sub> atmosphere. Thermogravimetric analysis (TGA) was done by Perkin Elmer STA 6000 at the heating rate 10 °C min<sup>-1</sup> from room temperature to 700 °C under N<sub>2</sub> atmosphere. Porosity of electrospun nanofibrous membranes was calculated by weighing membrane before and after absorbing *n*-butanol and knowing the density of *n*-butanol. The electrolyte uptake of polymer electrolyte membranes was calculated by soaking the membrane in lithium hexafluorophosphate (LiPF<sub>6</sub>), ethylene carbonate (EC) and dimethyl carbonate (DMC) solution. The ionic conductivity ( $\sigma$ ) of polymer electrolyte membranes was determined through an ionic conductivity cell, by sandwiching a given polymer electrolyte membrane between two stainless steel blocking electrodes (SS/polymer electrolyte membrane/SS, SS: stainless steel) using Zahner Zennium Electrochemical Analyzer at room temperature in frequency range between 10 mHz and 100 kHz with AC amplitude of 10 mV.

## Results and discussion

Figure 1 shows SEM images and histograms of electrospun (a) PVdF, (b) PVdF/PMMA (80–20), and (c) PVdF–PMMA (50–50) nanofibrous membranes. It can be seen from SEM images that the average fiber diameter decreases with increasing PMMA percentage from 0 to 50% in the composites. The average fiber diameter of PVdF, PVdF–PMMA (80:20) and PVdF–PMMA (50:50) is found to be 647, 183 and 179 nm, as shown in histograms Fig. 1d–f, respectively. This unique porous structure is beneficial for the electrolyte to penetrate and retain electrolyte effectively, and it facilitates an electrolyte to diffuse smoothly into the cell assembly.

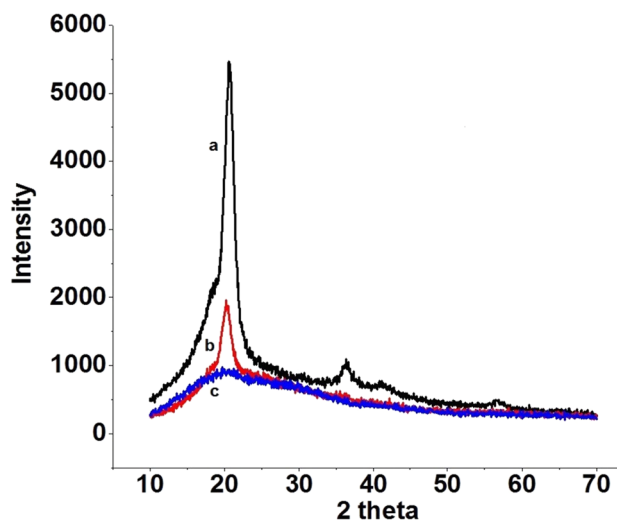
Figure 2 shows the FTIR spectra of electrospun PVdF, PVdF–PMMA (80–20) and PVdF–PMMA (50–50) nanofibrous membranes. It is observed from the figure that for pure PVdF, the characteristic bands are appeared at 1727, 1401, 1077, 1005, 884, 690 and 621  $\text{cm}^{-1}$ . The band at 1727  $\text{cm}^{-1}$



**Fig. 2** FTIR spectra of **a** PVdF, **b** PVdF–PMMA (80:20), and **c** PVdF–PMMA (50:50) nanofibrous membranes

assigned to stretching vibration of C=C. The band at 1401  $\text{cm}^{-1}$  is related to stretching vibration of  $\text{CF}_2$  group. The bands appearing at 1077 and 1005  $\text{cm}^{-1}$  are appeared due to scissoring vibration of  $\text{CF}_2$  group and stretching vibration of CH group, respectively. A band at 884  $\text{cm}^{-1}$  which shows the characteristic peak of vinylidene group of PVdF is assigned to C–F stretching. The bands at 690 and 621  $\text{cm}^{-1}$  are due to crystalline phase of PVdF and indicate out of plane C–H bending and bending vibration of  $\text{CF}_2$ . The characteristic bands for PVdF–PMMA (80:20) are appeared at 1721, 1398, 1181, 1027, 884, 695 and 621  $\text{cm}^{-1}$ . The band at 1721  $\text{cm}^{-1}$  is identified as C=O stretching vibration in the pendant group ( $-\text{COOCH}_3$ ) of PMMA. The characteristic peaks at 1398 and 884  $\text{cm}^{-1}$  are due to C–H bending vibration and  $-\text{CH}_2-$  stretching vibration [31]. It is observed that the intensity and peak position are slightly shifted due to blending of PMMA. These changes clearly indicate the miscibility of PVdF and PMMA. For PVdF–PMMA (50:50), it is found that new bands at 1446 and 1528  $\text{cm}^{-1}$  are appeared. The band at 1446  $\text{cm}^{-1}$  corresponds to  $\text{CH}_2$  wagging deformation of pure PVdF membrane. It can be seen that intensity of this peak increases with the addition of PMMA. The peak corresponding to 1734  $\text{cm}^{-1}$  in the PVDF/PMMA blend membrane is due to the carbonyl (C=O) group present in PMMA. This result suggests that there is a specific interaction between the carbonyl groups of PMMA and the  $\text{CH}_2$  groups of PVDF and indicates the formation of a PVDF/PMMA blend membrane.

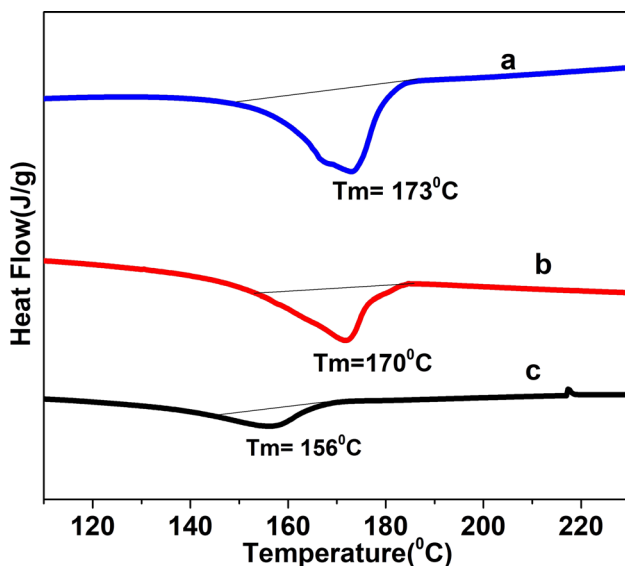
X-ray diffraction pattern helps to provide the influence of PMMA on structure of PVdF in the sample. Figure 3 shows the XRD patterns of PVdF, PVdF–PMMA (80–20) and PVdF–PMMA (50–50) nanofibrous membranes. PVdF membrane has sharp peaks at 20.7° (110) and 26.60° (022)



**Fig. 3** XRD patterns of **a** PVdF, **b** PVdF–PMMA (80:20), and **c** PVdF–PMMA (50:50) nanofibrous membranes

corresponding to orthorhombic  $\alpha$ -phase of PVdF [30]. These peaks have been suppressed in the PVdF–PMMA composites. PVdF–PMMA (80:20) shows a semicrystalline nature whereas PVdF–PMMA (50:50) shows amorphous nature. Thus, by adding more PMMA in PVdF composites, the crystallinity of PVdF decreases and PVdF–PMMA (50:50) blend becomes more amorphous which enhances greater ionic diffusion causes more ionic conductivity of the polymer electrolyte membrane.

Figure 4 shows the differential scanning calorimetric (DSC) curves of PVdF, PVdF–PMMA (80–20) and PVdF–PMMA (50–50) nanofibrous membranes. In DSC curves, melting temperature ( $T_m$ ) goes on decreasing from a to c. It is observed from figure that  $T_m$  for PVdF: PMMA (100:00) is 173 °C; it goes on decreasing with the incorporation of PMMA in PVdF. The value of  $T_m$  for PVdF–PMMA (80:20) and PVdF–PMMA (50:50) is 170 and 156 °C. The decrease in melting temperature is the indication of decreased crystallinity of polymer matrix in the polymeric system. It further leads to the improvement in the segmental motion of the polymeric chain and, thereby, enhances the ionic conductivity of polymer blend electrolytes. The absence of sharp glass transition and any additional peak for PVdF–PMMA blends confirm the miscibility of PMMA with PVdF in the polymer blends. The crystallinity ( $\chi_c\%$ ) of PVdF, PVdF–PMMA (80–20) and PVdF–PMMA (50–0) nanofibrous membranes was calculated from the crystalline melting heat of perfectly crystalline PVdF ( $\Delta H_f^* = 105 \text{ J/g}$ ), the melting enthalpy of the electrospun membranes ( $\Delta H_f$ ) in DSC curves determined from the integral area of the baseline using Eq. (1) [27] and listed in Table 1.



**Fig. 4** DSC curves of **a** PVdF **b** PVdF–PMMA (80:20) **c** PVdF–PMMA (50:50) nanofibrous membranes

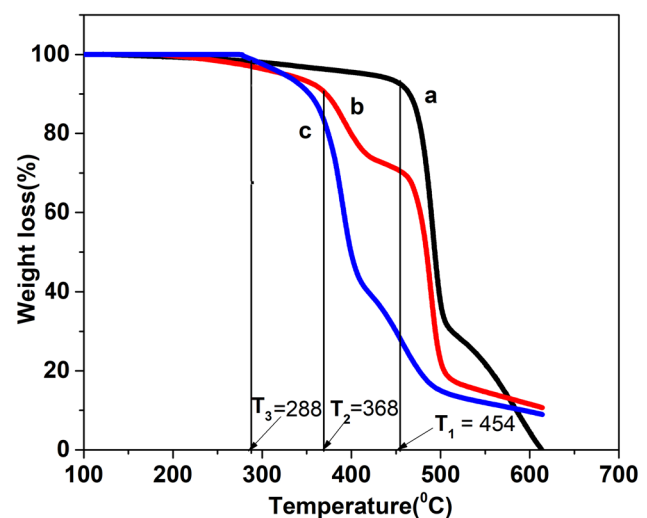
**Table 1** Melting enthalpy ( $\Delta H_f$ ), crystallinity ( $\chi_c$ ), bulk resistance ( $R_b$ ) and ionic conductivity ( $\sigma$ ) of PVdF, PVdF/PMMA (80:20) and PVdF/PMMA (50:50) nanofibrous membranes

Polymer membranes	$\Delta H_f$ (J/g)	$\chi_c$ (%)	$R_b$ ( $\Omega$ )	$\sigma$ (S/cm)
PVdF	53.29	50.75	0.50	0.10
PVdF:PMMA (80:20)	43.84	41.75	0.29	0.13
PVdF:PMMA (50:50)	25.33	24.12	0.22	0.15

$$\chi_c(\%) = \frac{\Delta H_f}{\Delta H_f^*} \times 100. \quad (1)$$

The evaluated crystallinity of PVdF–PMMA (50–50) membrane was found to be 24.12% as compared to 41.75% for PVdF–PMMA (80–20) and 50.75% for pure PVdF membrane. Hence, the prepared PVdF–PMMA (50–50) membrane has the lowest crystallinity means amorphous nature as confirmed from XRD. Lowest crystallinity of PVdF–MMA (50–50) nanofibrous membrane represents the membrane suitability towards potential separator in lithium ion battery due to high electrolyte uptake and ionic conductivity which helped for more migration of lithium ions through it.

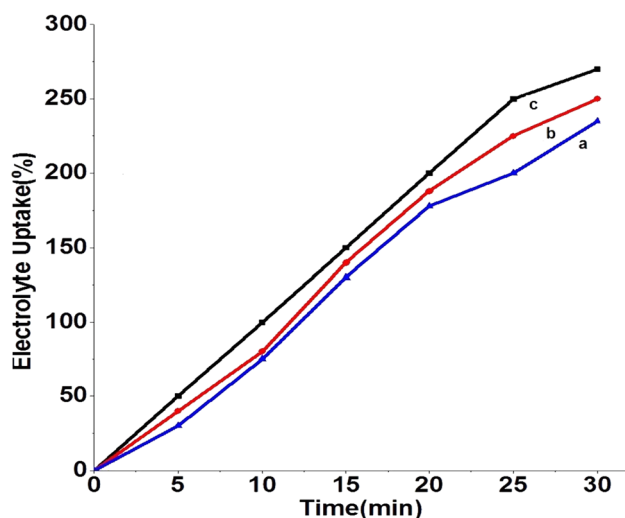
Figure 5 shows thermogravimetry (TGA) of PVdF, PVdF–PMMA (80–20) and PVdF–PMMA (50–50) nanofibrous membranes. It can be seen from the figure that the onset decomposition temperature of PVdF is 454 °C with a weight loss of 8%. The second decomposition occurs at 510 °C with a weight loss of about 70%. There are two decompositions on the TG curve of PVdF:PMMA (80:20). The first decomposition occurs at 368 °C with a weight loss of about 9% which may be due to decomposition of



**Fig. 5** Thermogravimetry (TGA) of **a** PVdF, **b** PVdF–PMMA (80–20) and **c** PVdF–PMMA (50–50) nanofibrous membranes

PMMA in the membrane. The second decomposition occurs at 430 °C with a weight loss of about 30%. A small weight loss 4% is observed for PVdF: PMMA (50:50) with first decomposition temperature at 288 °C and the second decomposition for the same composition occurs at 330 °C with a weight loss of about 30% which may be due to increase in content of PMMA in the membrane. These results indicate that the PVdF–PMMA membrane has a good thermal stability with minimum weight % loss.

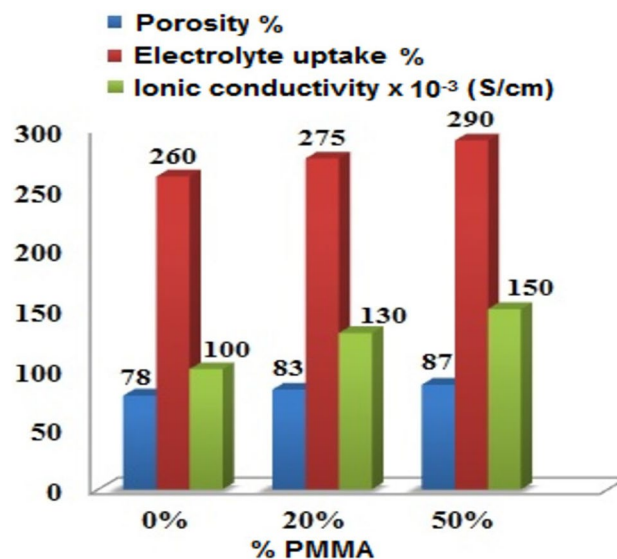
Porosity of the prepared PVdF, PVdF–PMMA (80–20) and PVdF–PMMA (50–50) nanofibrous membranes was determined by *n*-butanol uptake method. Nanofibrous membranes were immersed in *n*-butanol for 2 h. The porosity % of PVdF, PVdF–PMMA (80:20) and PVdF–PMMA (50:50) nanofibrous membrane was found to be 78, 83 and 87%, respectively. The high porosity was reflected to explain the high electrolyte uptake of polymer electrolytes. The electrolyte uptake behavior of the electrospun PVdF, PVdF–PMMA (80:20) and PVdF–PMMA (50:50) membrane was recorded after every 5 min by soaking the electrospun membranes in the liquid electrolyte 1 M LiPF<sub>6</sub>/EC:DMC (1:1 v/v) solution for 30 min. The electrolyte uptake was calculated by measuring weight of electrospun membrane before and after absorbing the electrolyte solution [27]. The PVdF, PVdF–PMMA (80:20) and PVdF–PMMA (50:50) membranes showed an electrolyte uptake of about 260, 275 and 290% within 30 min (Fig. 6). It is observed from the data that electrolyte uptake % increases with increasing PMMA percentage. The unique fibrous structure of the membranes induces fast liquid penetration to form the polymer electrolyte with interpenetrating polymer network within 30 min. The higher electrolyte uptake of PVdF–PMMA (50:50) membrane could make an improvement of ionic conductivity suitable as separator



**Fig. 6** Electrolyte uptake of **a** PVdF, **b** PVdF–PMMA (80:20), and **c** PVdF–PMMA (50:50) nanofibrous membranes

for lithium ion battery. The porosity, electrolyte uptake and ionic conductivity of PVdF, PVdF–PMMA (80:20) and PVdF–PMMA (50:50) nanofibrous membranes are shown in Fig. 7. The Nyquist plot of PVdF, PVdF–PMMA (80:20) and PVdF–PMMA (50:50) nanofibrous polymer electrolyte membranes at room temperature is shown in Fig. 8. The bulk resistance ( $R_b$ ) of the polymer electrolyte membranes was determined from the intercept of the extended impedance plots with the *x* axis from the Nyquist plots. The bulk resistance was found to be decreasing with increasing % of PMMA in PVdF. The enhancement in ionic conductivity was attributed mainly due to higher electrolyte uptake obtained by porous structure and decrease in crystallinity by adding PMMA in PVdF. Bulk resistance and ionic conductivity of PVdF, PVdF–PMMA (80:20) and PVdF–PMMA (50:50) nanofibrous polymer electrolyte membranes are listed in Table 1. The nanofibrous membranes obtained by the process of electrospinning had fully interconnected porous structures with decrease in diameter by increasing PMMA percentage in PVdF.

Battery performance was conducted by fabricating Swagelok (Li/PE/LiFePO<sub>4</sub>) cells by placing as-fabricated nanofibrous polymer electrolyte (PE) membranes between lithium metal anode and lithium iron phosphate (LiFePO<sub>4</sub>) cathode [8, 29]. The fabrication of test cells was carried out in a glove box. The electrochemical tests of the Li/PE/LiFePO<sub>4</sub> cells were conducted in an automatic galvanostatic charge–discharge unit, battery cyler (Arbin BT 2000) at room temperature at the current rate of 0.1 °C. The charge–discharge process was performed between 2.6 and 4.3 V [30]. Figure 9 shows 1st cycle of charge and discharge



**Fig. 7** Porosity, electrolyte uptake and ionic conductivity of PVdF, PVdF–PMMA (80:20) and PVdF–PMMA (50:50) nanofibrous membranes

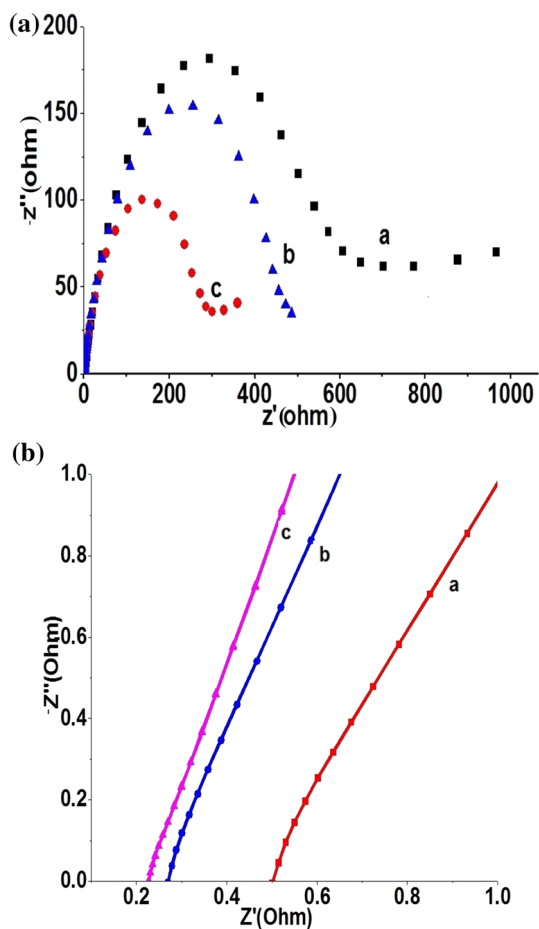


Fig. 8 Nyquist plot of a PVdF, b PVdF–PMMA (80:20) and c PVdF–PMMA (50:50) nanofibrous polymer electrolyte membranes

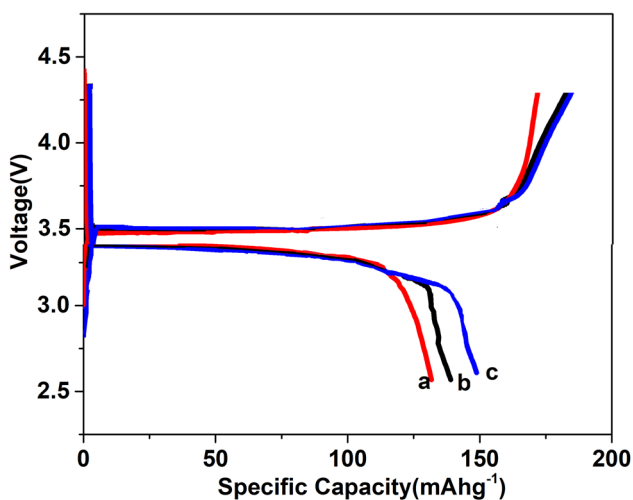


Fig. 9 1st cycle of charge and discharge curves of Swagelok cells with a PVdF, b PVdF–PMMA (80:20), and c PVdF–PMMA (50:50) nanofibrous polymer electrolyte membranes

curves of fabricated Swagelok (Li/PE/LiFePO<sub>4</sub>) cells. The initial discharge capacity was found to be 138.4, 144.7 and 150.3 mAh/g for separators of PVdF, PVdF/PMMA (80:20) and PVdF/PMMA (50:50) membranes, respectively. Compared with cells of different PEs, discharged capacity for the cell with PVdF–PMMA (50:50) separator was found to be relatively high cathode utilization corresponding to 88.4% of theoretical capacity. Moreover, the PVdF/PMMA (50:50) nanofibrous polymer electrolyte membrane showed a slightly higher discharge capacity than that of PVdF and PVdF/PMMA (80:20) due to higher ionic conductivity. The cycle performance of the cells with the polymer electrolytes based on PVdF, PVdF–PMMA (80:20) and PVdF–PMMA (50:50) membranes is shown in Fig. 10. Even after 50 cycles, the discharge capacity of PVdF/PMMA (50:50) membranes was found to be 140 mAh/g. This shows that 93.3% of its initial discharge capacity was retained compared to other polymer electrolytes. This indicates that the discharge capacity has a good retention even after 50 cycles. These results suggest that PVdF–PMMA (50:50) nanofibrous polymer electrolyte membrane is a potential separator for lithium ion battery.

### Conclusions

PVdF–PMMA composite fibers with diameter in nanoscale membranes were successfully prepared by electrospinning. PVdF–PMMA composites membranes showed excellent electrochemical properties due to the interconnected porous structure. The increase in percentage of PMMA enhances electrolyte uptake and ionic conductivity of PVdF–PMMA composites membranes. Among PVdF–PMMA membranes

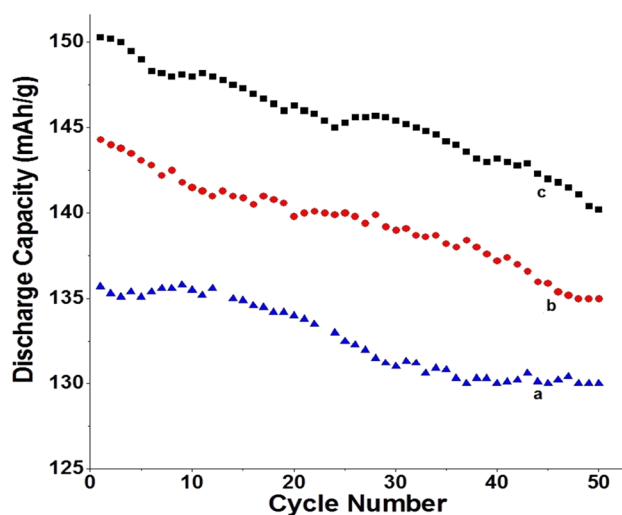


Fig. 10 Cycle performance of Swagelok cells with a PVdF, b PVdF–PMMA (80:20) and c PVdF–PMMA (50:50) nanofibrous polymer electrolyte membranes

studied, PVdF–PMMA (50:50) membrane exhibited the highest porosity, electrolyte uptake, ionic conductivity, and discharge capacity retention. These results suggested that the preparation methodology for PVdF/PMMA composites membranes by electrospinning with PVdF/PMMA (50:50) nanofibrous polymer electrolyte membrane was found to be potential and promising separator for lithium ion batteries than that of pure PVdF and PVdF–PMMA (80:20).

**Acknowledgements** This work was supported by the Department of Science and Technology (DST, New Delhi, India) Support under DST-FIST Program, Grant no. SR/FST/PSI-178/2012(C).

**Open Access** This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

## References

- Kim, M., Park, J.H.: Multi-scale pore generation from controlled phase inversion: application to separators for Li-ion batteries. *Adv. Energy. Mater.* **3**, 1417–1420 (2013)
- Zhao, Y., Wu, C., Peng, G., Chen, X., Yao, X., Bai, Y., Wu, F., Chen, S., Xu, X.: A new solid polymer electrolyte incorporating  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  into a polyethylene oxide matrix for all-solid-state lithium batteries. *J. Power Source* **301**, 47–53 (2016)
- Shi, Q., Yu, M., Zhou, X., Yan, Y., Wan, R.C.: Structure and performance of porous polymer electrolytes based on P(VDF–HFP) for lithium ion batteries. *J. Power Sources* **103**, 286–292 (2001)
- Magistris, A.A., Quartarone, E., Mustarelli, P., Saito, Y., Kataoka, H.: PVdF based porous polymer electrolytes for lithium batteries. *Solid State Ion.* **152**, 347–354 (2002)
- Song, J.M., Kang, H.R., Kim, S.W., Lee, W.M., Kim, H.T.: Electrochemical characteristics of phase-separated polymer electrolyte based on poly(vinylidene fluoride-*co*-hexafluoropropane) and ethylene carbonate. *Electrochim. Acta* **48**, 1339–1346 (2003)
- Kalyana, N.T., Subramania, A.: Microstructure of PVdF-*co*-HFP based electrolyte prepared by preferential polymer dissolution process. *J. Membr. Sci.* **289**, 1–6 (2007)
- Zhu, Y.S., Wang, F.X., Liu, L.L., Xiao, S.Y., Yang, Q.Y.: Composite of a nonwoven fabric with poly(vinylidene fluoride) as a gel membrane of high safety for lithium ion battery. *Energy Environ. Sci.* **6**, 618–624 (2013)
- Lv, R., Zhu, Y., Liu, H., Na, B., Huang, Y., Xie, X.: Poly(vinylidene fluoride)/poly(acrylonitrile) blend fibrous membranes by centrifugal spinning for high-performance lithium ion battery separators. *J. Appl. Polym. Sci.* **134**(44515), 1–7 (2017)
- Muthuvinnayagam, M., Gopinathan, C.: Characterization of proton conducting polymer blend electrolytes based on PVdF–PVA. *Polymer* **68**, 122–130 (2015)
- Gentili, V., Panero, S., Reale, P., Scrosati, B.: Composite gel-type polymer electrolytes for advanced, rechargeable lithium batteries. *J. Power Sources* **170**, 185–190 (2007)
- Raghavan, P., Zhou, X., Manuel, J., Chauhan, G., Ahn, J., Rya, H., Ahn, H.: Electrochemical performance of electrospun poly(vinylidene fluoride-*co*-hexafluoropropylene)-based nanocomposite polymer electrolytes incorporating ceramic fillers and room temperature ionic liquid. *Electrochim. Acta* **55**, 1347–1354 (2010)
- Wang, Y.J., Kim, D.: Crystallinity, morphology, mechanical properties and conductivity study of in situ formed PVdF/LiClO<sub>4</sub>/TiO<sub>2</sub> nanocomposite polymer electrolytes. *Electrochim. Acta* **52**, 3181–3189 (2007)
- Pu, W.H., He, X.M., Wang, L., Jiang, C.Y., Wan, C.R.: Preparation of PVDF–HFP microporous membrane for Li-ion batteries by phase inversion. *J. Membr. Sci.* **272**, 11–14 (2006)
- Zhao, Y.H., Xu, Y.Y., Zhu, B.K.: Effect of amphiphilic hyperbranched-star polymer on the structure and properties of PVDF based polymer electrolytes. *Solid State Ion.* **180**, 1517–1523 (2007)
- Li, Z., Zhang, H., Zhang, P., Li, G.C., Wu, Y., Zhou, X.D.: Effects of the porous structure on conductivity of nanocomposite polymer electrolyte for lithium ion batteries. *J. Membr. Sci.* **322**, 416–422 (2008)
- Miao, R., Liu, B., Zhu, Z., Liu, Y., Li, J., Wang, X., Li, Q.: PVDF–HFP-based porous polymer electrolyte membranes for lithium ion batteries. *J. Power Sources* **184**, 420–426 (2008)
- Liu, F., Hashim, N.A., Liu, Y., Moghareh, M.R., Li, K.: Progress in the production and modification of PVDF membranes. *Membr. Sci.* **375**, 1–27 (2011)
- Choi, E.S., Lee, S.Y.: Particle size-dependent, tunable porous structure of a SiO<sub>2</sub>/poly(vinylidene fluoride-hexafluoropropylene)-coated poly(ethylene terephthalate) nonwoven composite separator for a lithium-ion battery. *Mater. Chem.* **21**, 14747–14753 (2011)
- Kim, Y.J., Ahn, C.H., Lee, M.B., Choi, M.S.: Characteristics of electrospun PVDF/SiO<sub>2</sub> composite nanofiber membranes as polymer electrolyte. *Mater. Chem. Phys.* **127**, 137–142 (2011)
- Masoud, E.M.: Nano lithium aluminate filler incorporating gel lithium triflate polymer composite: preparation, characterization and application as an electrolyte in lithium ion batteries. *Polym. Test.* **56**, 65–73 (2016)
- Rhoo, H.J., Kim, H., Park, J., Hwang, T.: Ionic conduction in plasticized PVC/PMMA blend polymer electrolytes. *Electrochim. Acta* **42**, 1557–1579 (1997)
- Ma, X., Huang, X., Gao, J., Zhang, S., Deng, Z., Suo, J.: Compliant gel polymer electrolyte based on poly(methyl acrylate-*co*-acrylonitrile)/poly(vinyl alcohol) for flexible lithium-ion batteries. *Electrochim. Acta* **115**, 216–222 (2014)
- Li, Z.M., Wei, J.G., Shan, F., Yang, J., Wang, X.L.: PVDF/PMMA brushes membrane for lithium-ion rechargeable batteries prepared via pre-irradiation grafting technique. *J. Polym. Sci. B Polym. Phys.* **46**, 751–758 (2008)
- Idris, N., Rahman, M.M., Wang, J.Z., Liu, H.K.: Microporous gel polymer electrolytes for lithium rechargeable battery application. *J. Power Sources* **201**, 294–300 (2012)
- He, X., Shi, Q., Zhou, Q., Wan, C., Jiang, C.: In situ composite of nano SiO<sub>2</sub>–P(VDF–HFP) porous polymer electrolytes for Li-ion batteries. *Electrochim. Acta* **51**, 1069–1075 (2005)
- Cui, W.W., Tang, D.Y., Gong, Z.L.: Electrospun poly(vinylidene fluoride)/poly(methyl methacrylate) grafted TiO<sub>2</sub> composite nanofibrous membrane as polymer electrolyte for lithium-ion batteries. *J. Power Sources* **223**, 206–214 (2013)
- Xiao, Q.Z., Li, Z.H., Gao, D.S., Zhang, H.L.: A novel sandwiched membranes as polymer electrolyte for application in lithium ion battery. *J. Membr. Sci.* **326**, 260–264 (2009)
- Li, X., Cao, Q., Wang, X., Jiang, S., Deng, H., Wu, N.: Preparation of poly(vinylidene fluoride)/poly(methyl methacrylate) membranes by novel electrospinning system for lithium ion batteries. *J. Appl. Polym. Sci.* **122**, 2616–2620 (2011)



29. Mahant, Y.P., Kondawar, S.B., Bhute, M., Nandanwar, D.V.: Electrospun poly(vinylidene fluoride)/poly(methyl methacrylate) composite nanofibers polymer electrolyte for batteries. *Proced. Mater. Sci.* **10**, 595–602 (2015)
30. Padmaraj, O., Venkateswarlu, M., Satyanarayana, N.: Characterization and electrochemical properties of (PVdF-*co*-HFP) based electrospun nanocomposite fibrous polymer electrolyte membrane for lithium battery applications. *Electroanalysis* **26**, 2373–2379 (2014)
31. Zhang, H., Lin, C.E., Zhou, M.Y., John, A.E., Zhu, B.K.: High thermal resistance polyimide separators prepared via soluble

precursor and non-solvent induced phase separation process for lithium ion batteries. *Electrochim. Acta* **187**, 125–133 (2016)

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.