



DEVELOPMENT OF ELECTROSPUN PVDF-PMMA-PS BLEND POLYMER ELECTROLYTE MEMBRANE FOR LITHIUM ION BATTERY

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ABSTRACT

In this paper fabrication of nanofibrous blend polymer electrolyte membranes of poly (vinylidene fluoride) (PVdF), poly (methyl methacrylate) (PMMA) and polystyrene (PS) with different proportion of PMMA and PS (PVdF: PMMA:PS = 100:00:00, 80:20:00 and 80:15:05) were fabricated by electrospinning, to investigate the influence of PMMA and PS on lithium ion battery performance. The prepared blend polymer electrospun nanofibrous membranes were characterized by SEM, FTIR and XRD for morphology, structure and crystallinity. The thermal and crystalline properties were characterized by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC). PVdF-PMMA-PS (80:15:05) polymer electrolyte membrane showed ionic conductivity 2.50×10^{-2} S/cm and electrolyte uptake 544% at room temperature. The electrolyte uptake, ionic conductivity, and discharge capacity retention were improved by optimizing the proportion of PMMA and PS in PVdF. Nanofibrous PVdF: PMMA: PS (80:15:05) blend polymer electrolyte membrane was found to be a potential separator for lithium ion batteries.

Keywords: Poly (vinylidene fluoride), Poly(methyl methacrylate), Polystyrene, Polymer electrolyte, Electrospinning, Nanofibers, Lithium ion batteries,

1. Introduction

The rechargeable lithium battery has attracted great attention due to high energy and power density, good rate capability and low maintenance (Minami, Gellings, Zoski,

Bagotsky and Keihne). These batteries are commonly used in portable devices that require low volume and weight, such as laptop computers, mobile phones strong military equipment, electric vehicles etc. (Owen and Long). Lithium ion batteries have advantages like compact size, light weight, high energy density, high depth of discharge, low self-discharge, long cycle life, etc

Polymer electrolyte membrane is one of the most important parts in the development of Li-ion batteries. Characteristics of a membrane is determined by the chemical stability, mechanical strength, stable shape, wettability, porosity, permeability, thickness, thermal shrinkage, shut down, and cost. Polymer electrolyte membranes are prepared by immobilization of organic liquid electrolytes into polymer host (Subramania). The membrane should have the capability to absorb the liquid electrolyte without leakage, be chemically compatible with electrode materials and hold well to the electrodes. Poly (ethylene oxide) (PEO), polyacrylonitrile (PAN), poly (methyl methacrylate) (PMMA), poly (vinylidene fluoride) (PVDF), poly (vinyl alcohol) (PVA) and poly (vinylidene fluoride-cohexafluoro propylene) (PVDF-HFP) have been studied as host polymer for fabricating nanofibrous polymer electrolyte membrane (Zhu, Lv, Muthuvinaayagam, Gentili, Raghavan, Wang, Pu, Zhao, Zhang and Miao). The process of electrospinning is particularly suitable for producing thin and homogenous polymer membranes with pores in the nano- to micrometer size range. Since the membranes possess high porosity, they also exhibit a high electrolyte uptake that results in an increase in ionic conductivity (Shi).

Polyvinylidene fluoride (PVdF) is a thermoplastic polymer that has physical properties such as high polarity, excellent thermal and mechanical properties, and high affinity to an electrolyte solution, good chemical stability, low density (1.78 g/cm³) and excellent compatibility with electrodes which make PVdF to be used as a separator membrane in lithium-ion polymer battery (Liu). It also has strong electron-withdrawing functional groups (-C-F) to induce a net dipole moment with high dielectric constant ($\epsilon = 8.4$) which supports high concentration of charge carriers (Li). It is a semi-crystalline polymer having excellent film-forming ability and thermal stability (Choi). PVdF is a semi-crystalline polymer the crystalline domains of PVdF restrict the penetration of liquid electrolytes and the movement of lithium ions from cathode to anode and vice versa. Also, PVdF is soluble in liquid electrolytes which are used for the preparation of polymer electrolytes (Rho). Therefore batteries with PVdF based polymer electrolyte show low ionic conductivity (Kim).

Polymethyl methacrylate (PMMA) is an amorphous polymer with an excellent life period and good mechanical properties. PMMA based polymer electrolytes are less reactive towards the lithium electrode. Moreover, MMA (methyl methacrylate) monomer in PMMA has a polar functional group in the main polymer chain that has high affinity for lithium ions, which are transported. Oxygen atoms from the MMA structure will form a coordinate bond with the lithium ion from doping salts. Hence, the increase in effective ionic transport of PMMA based polymer electrolytes may be due to the presence of the polar functional group in PMMA. It is a common thermoplastic polymer. Its amorphous structure is beneficial to ionic conduction. PMMA-based gel electrolytes have shown excellent interfacial stability towards lithium metal, high electrolyte uptake, high ionic conductivity and good electrochemical stability (Rho). PMMA has ability to make chemical cross-linking, which will remarkably increase the mechanical strength and the electrolyte solution retention ability of the polymer electrolyte (Ma and Liu). Also it has been reported that gel electrolytes based on cross-linked PMMA can suppress lithium dendrite formation (He).

Polystyrene (PS) is an amorphous polymer

having higher T_g (100 °C) and good thermal stability. It possesses excellent mechanical properties: high strength, fatigue resistance and dimension stability. PS was used in blends with other polymer to provide toughness to the blend (Cui). At higher temperatures, the backbone of PS starts to slide past each other. This makes PS flexible and stretchable. This quality is coupled with the strength of PVdF to develop a tough yet stronger membrane. The aromatic ring in PS also disallows a certain extent of crystallization, which will be useful to enhance the easy transportation of Li⁺ ions. This means, the resultant polymer blended membrane can be expected to have more flexibility and ionic conductivity at room temperature. The advantage of blending PS with PMMA as polymer electrolyte is believed best as PMMA has high electrolyte uptake, high ionic conductivity and has good electrochemical stability which enhances the mechanical strength of the polymer electrolyte membrane (He and Cui). The polymer blends electrolyte membrane of PVdF, PMMA and PS provides enhancement on the ionic conductivity, electrochemical stability and cycling performance of battery separators.

In this work, the fabrication of polymer nanofibrous electrolyte membranes of PVdF-PMMA-PS composites in different proportion of PMMA and PS (PVdF: PMMA: PS = 100:00:00, 80:20:00, 80:10:10 and 80:00:20) by electrospinning is reported to investigate the influence of PMMA and PS on lithium ion battery performance. The effect of concentration of PMMA and PS in composites on morphology, ionic conductivity, porosity and discharge capacity retention for lithium ion battery separator is studied and systematically compared.

1.1 Experimental

PVdF-PMMA-PS composites were prepared with varying weight ratio of PMMA and PS in PVdF. The total polymer concentration was fixed at 15 wt%. PVdF-PMMA-PS composites nanofibrous membranes in different proportion of PVdF, PMMA and PS were prepared by electrospinning. In a typical procedure for the preparation of PVdF-PMMA-PS (80:15:05) nanofibrous membrane, 15% PVdF-PMMA-PS (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 0.4 ml/h, electric field 20 kV and distance 18 cm between the syringe needle and grounded collector (aluminium 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-PS (80:20:00) and PVdF-PMMA-PS (100:00:00) abbreviated as pure PVdF have been prepared by electrospinning with the same operating conditions. PVdF-PMMA-PS nanofibrous polymer electrolytes were prepared by immersing the electrospun nanofibrous membranes in 1 M LiPF₆ (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.

1.2 Characterizations

The surface morphology of electrospun nanofibrous membranes was studied by scanning electron microscope (CARL ZEISS EVO-18). Fourier transform infrared (FTIR) spectra of electrospun nanofibrous membranes were obtained on α -Bruker model. X-ray diffraction (XRD) patterns of electrospun nanofibrous membranes were reported on Rigaku Miniflex II Desktop X-ray diffractometer. The crystallinity of electrospun nanofibrous membranes was obtained using differential scanning calorimetry (DSC) (Mettler Toledo DSC 822 e) with heating rate 10 °C per min under N₂ atmosphere. Thermogravimetric analysis (TGA) was done by Perkin Elmer STA 6000 at the heating rate 10 °C min⁻¹ from room temperature to 700 °C under N₂ atmosphere. Porosity of electrospun membrane, 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 (LiPF₆), ethylene carbonate (EC) and dimethyl carbonate (DMC) solution. The ionic conductivity (σ^{-1}) 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 10mV.

1.3 Results and discussion

Figure 1 shows SEM images and histograms of electrospun (a) PVdF:PMMA:PS (100:00:00) (b) PVdF:PMMA:PS (80:20:00) and (c) PVdF:PMMA:PS (80:15:05) nanofibrous membrane. The average fiber diameter of PVdF, PVdF:PMMA:PS (80:20:00) and PVdF:PMMA:PS (80:15:05) is found to be 647, 183 and 157nm, as shown in histograms respectively. It is found that, with the addition of PMMA and PS, the fibre diameter decreases. It can be seen that long, uniform and bead free fibers are obtained by electrospinning. The mean diameter of the electrospun membrane is calculated to 157nm. It is observed that with the addition of PMMA and PS in PVdF the diameter of fibre decreases. 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.

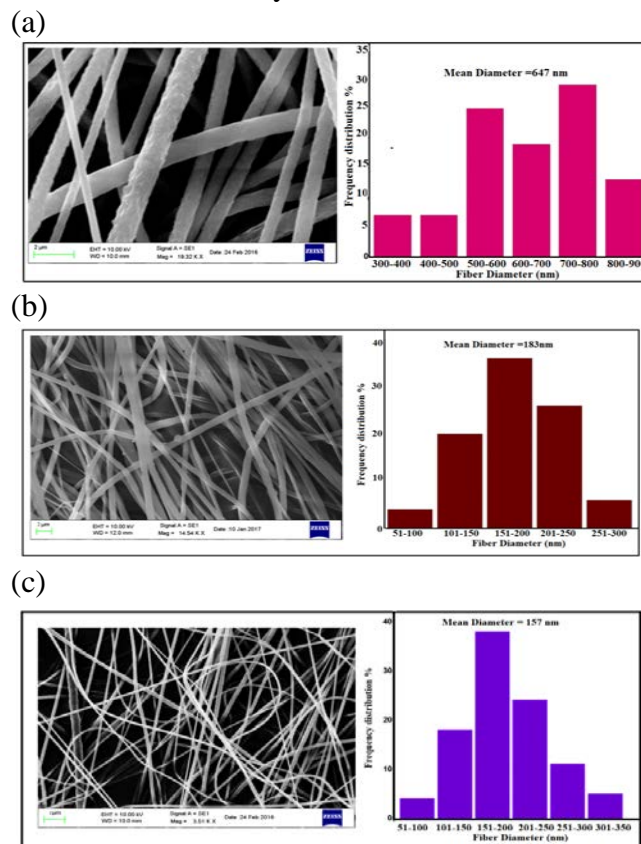


Figure (1) SEM image of (a) PVdF: PMMA: PS (100:00:00) (b) PVdF:PMMA:PS (80:20:00) (c) PVdF: PMMA: PS (80:15:05)

Figure 2 shows the FTIR spectra of electrospun (a) PVdF:PMMA: PS (100:00; 00) (b) PVdF:PMMA:PS (80:20:00) and (c) PVdF:PMMA:PS

(The spectra show the characteristic vibration bands at 1727,1401,1077,1005,884,690 and 621cm⁻¹. A band at 1727cm⁻¹ assigned to stretching vibration of C=C(Jaleh). An absorption peak at 1401 cm⁻¹ is related to stretching vibration of CF₂ group.The bands appearing at 1077cm⁻¹ and 1005 cm⁻¹ are appeared due to scissoring vibration of CF₂ group and stretching vibration of CH group respectively (Pavia and Saikia). A band at 884 cm⁻¹ which shows the characteristic peak of vinylidene group of PVdF, is assigned to C-F stretching. The absorption peaks at 690 cm⁻¹ and 621 cm⁻¹ are appeared due to crystalline phase of PVdF and indicates out of plane C-H bending and bending vibration of CF₂. All these bands match with the previously reported FTIR values for PVdF nanofibrous membrane (Pavia and Saikia)80:15:05) nanofibrous membrane.

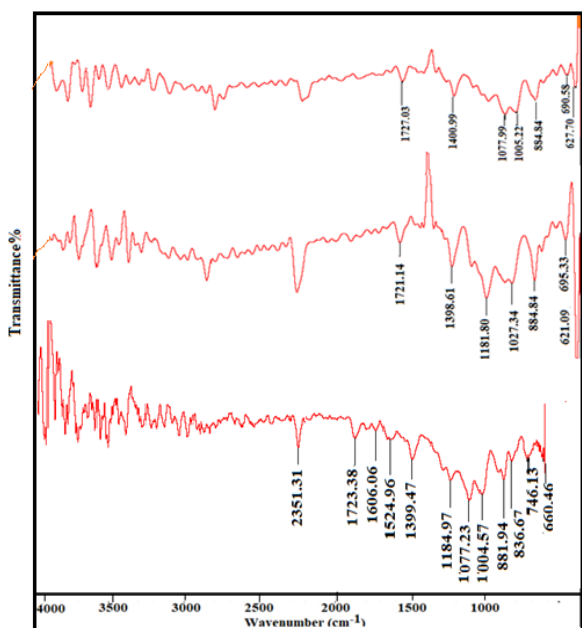


Figure 2 FTIR spectra of electrospun (a) PVdF:PMMA: PS (100:00; 00) (b) PVdF:PMMA:PS (80:20:00) and (c) PVdF:PMMA:PS(80:15:05)

It is also observed from the figure that in PVdF: PMMA: PS (80:20:00) the characteristic peaks are appeared at 1721,1398,1181,1027,884,695 and 621cm⁻¹. A peak at 1721cm⁻¹ is identified as C=O stretching vibrations in the pendant group (-COOCH₃) of PMMA.The characteristic peaks at 1398 and 884 cm⁻¹are appeared due to C-H bending vibration and –

CH₂- stretching vibration (Benabid).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.It can be seen from the figure that upon incorporation of PS in the polymer blend, the peak position is again shifted. In addition to that, new peaks are also observed at 1606cm⁻¹ and 1524cm⁻¹ which are due to CH deformation vibration in PS. Shifting of peaks position is the indication of strong polymer interaction in blend polymer nanofibrous membrane. It is observed from the figure that the existence of new peak along with original peak in the FTIR spectra confirms the miscibility of polymers.

X-ray diffraction pattern helps to provide the influence of PMMA on structure of PVdF in the sample. Figure 3 shows the XRD patterns (a) PVdF: PMMA: PS (100:00; 00) (b) PVdF:PMMA:PS (80:20:00) and (c) PVdF:PMMA:PS (80:15:05) nanofibrous membrane. It is observed from the figure 3 that a very strong diffraction peak for PVdF membrane is observed at 2 Θ of 20.81⁰ which corresponds to 110 and 200 reflections of β phase (Saikia). This confirms the partial crystallization of PVdF units and hence it shows the typical characteristics of a semicrystalline morphology of the polymer or in another word it can be said that it shows the coexistence of mixed crystalline and amorphous behaviour of the polymer. It has been observed from figure 3(b) and 3. (c) that, when PVdF is blended with PMMA and PS, no additional peaks appear in XRD pattern. The intensity of crystalline peak decreases and gets broadened, suggesting decrease in the crystallinity of the blend nanofibrous membrane. The absence of sharp Bragg peaks and the presence of broader peaks in XRD pattern of blend nanofibrous membrane show predominant amorphous nature of the blend nanofibrous membrane. Compared to diffraction peak of PVdF, a peak shift to the lower side and widening of the diffraction intensity of the peak is observed when PVdF is blended with PMMA and PS.In PVdF: PMMA: PS blend nanofibrous membrane, the relatively wider diffraction peak for PMMA and PS reflects the amorphous nature of the polymers. The peak is wider for PVdF: PMMA: PS (80:15:05) composition showing the amorphous nature of the blend nanofibrous membrane.

Thus, by adding PMMA and PS in PVdF, the crystallinity of PVdF decreases and PVdF:PMMA:PS (80:15:05) blend becomes more amorphous which enhances greater ionic diffusion causes more ionic conductivity of the polymer electrolyte membrane.

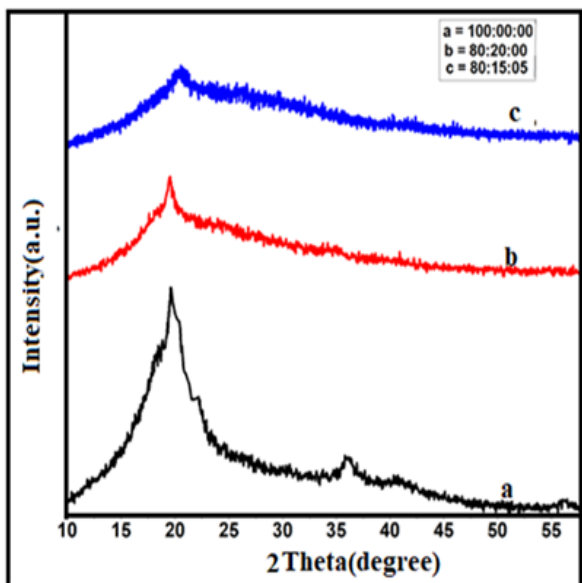


Figure 3 XRD of (a) PVdF: PMMA: PS (100:00:00) (b) PVdF:PMMA:PS(80:20:00) (c) PVdF: PMMA: PS (80:15:05)

Figure 4 shows the differential scanning calorimetric (DSC) curves of (a) PVdF:PMMA:PS (100:00; 00) (b) PVdF:PMMA:PS (80:20:00) and (c) PVdF:PMMA:PS (80:15:05) nanofibrous membrane. The melting temperature of PVdF:PMMA:PS (80:20:00) blend membrane is shifted from 173 °C to 171 °C by blending with PMMA. By adding PMMA and PS in PVDF the value melting temperature again decreases. For PVdF:PMMA:PS (80:15:05) blend nanofibrous membrane the melting temperature is 166.70C. It is observed from the graph that by adding PMMA and PS in PVdF the melting temperature decreases. 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 crystallinity % for PVdF:PMMA:PS blend nanofibrous membrane is calculated using eq.1.

$$Xc(\%) = \frac{\Delta H_f}{\Delta H_f^*} \times 100 \text{ -----1}$$

from the crystalline melting heat of perfectly crystalline PVdF ($\Delta H_f^* = 105 \text{ J/g}$), the melting

enthalpy of the electrospun membranes (ΔH_f) in DSC curves determined from the integral area of the baseline.

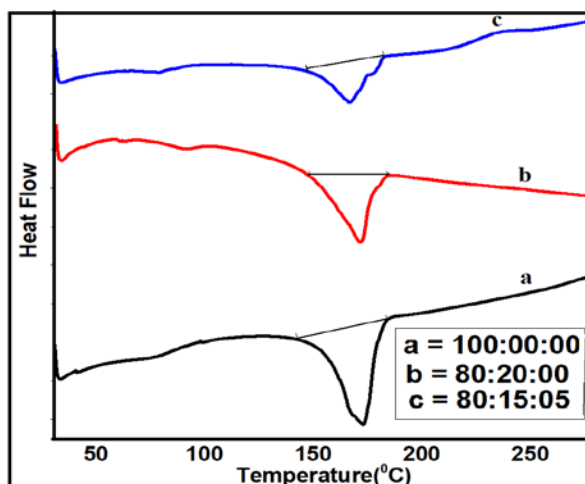


Figure 4 DSC curve of (a) PVdF: PMMA: PS (100:00:00) (b) PVdF: PMMA: PS (80:20:00) (c) PVdF: PMMA: PS (80:15:05)

Table 1

Polymer membrane	Tm (°C)	ΔH_f	χ_c (%)
PVdF:PMMA:PS (100:00:00)	173	53.2	50.29
PVdF:PMMA:PS (80:20:00)	171	43.8	41.75
PVdF:PMMA:PS (80:15:05)	166.7	37.9	36.14

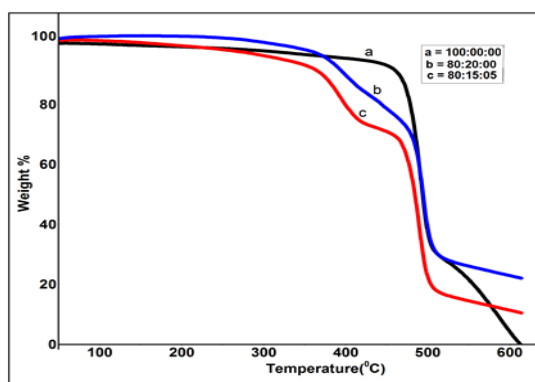


Figure 5 TGA curve of (a) PVdF: PMMA: PS (100:00; 00) (b) PVdF: PMMA: PS (80:20:00) and (c) PVdF: PMMA: PS (80:15:05) nanofibrous membrane

Figure 5 shows thermogravimetry (TGA) of (a) PVdF:PMMA:PS (100:00; 00) (b) PVdF:PMMA:PS (80:20:00) and (c) PVdF:PMMA:PS (80:15:05) nanofibrous membrane. It can be seen from the figure (a) and (b) that the onset decomposition temperature of PVdF is 314 °C with a weight loss of 8%. The second

decomposition occurs at 500⁰C with a weight loss of about 70%. There are two decompositions on the TG curve of PVdF: PMMA: PS (80:20:00). The first decomposition occurs at 367⁰C with a weight loss of about 10% which may be due to decomposition of PMMA in the membrane. The second decomposition occurs at 430⁰C with a weight loss of about 30%. A small weight loss 3% is observed for PVdF: PMMA: PS (80:15:05) with increase in the first decomposition temperature at 375⁰C and the second weight loss is 18 % with decomposition temperature 460⁰C 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:PMMA:PS (100:00:00), PVdF:PMMA:PS (80:20:00) and PVdF:PMMA:PS (80:15:05) nanofibrous membranes was determined by n-butanol method. Prepared nanofibrous membranes were immersed in n-butanol for 2 h. The porosity % of PVdF:PMMA:PS (100:00:00), PVdF:PMMA:PS(80:20:00) and PVdF:PMMA:PS (80:15:05) nanofibrous membrane was found to be 72%, 82% and 88% respectively.

Such large porosity will help the liquid electrolyte to more easily penetrate into sample with subsequently more liquid electrolyte embedded in the pores of the membrane which is enough to trap more liquid electrolyte and provide a path for ion migration. The high porosity can be used to explain the high electrolyte uptake of polymer electrolyte membrane. The electrolyte uptake behaviour of the electrospun PVdF:PMMA:PS (100:00:00), PVdF:PMMA:PS (80:20:00) and PVdF:PMMA:PS (80:15:05) nanofibrous membrane was calculated after every 5 min by soaking the electrospun membranes in the liquid electrolyte 1 M LiPF₆/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:PMMA:PS (100:00:00), PVdF:PMMA:PS (80:20:00) and PVdF:PMMA:PS (80:15:05) membranes showed an electrolyte uptake of about 509, 524 and 544 % within 30 min (Fig. 6). It is observed from the data that electrolyte uptake

% increases by adding PMMA and PS in PVdF.

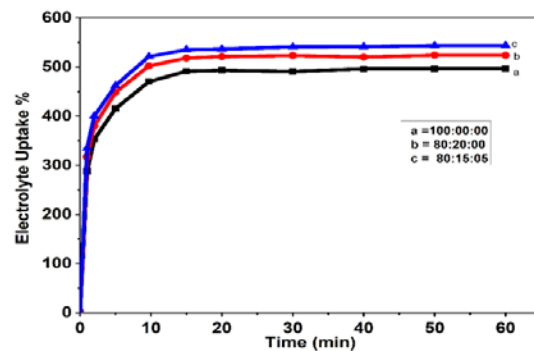


Figure 6 Electrolyte Uptake of a) PVdF: PMMA: PS (100:00; 00) (b) PVdF: PMMA: PS (80:20:00) and (c) PVdF: PMMA: PS (80:15:05) nanofibrous membrane

The Nyquist plot of PVdF: PMMA: PS (100:00:00), PVdF: PMMA:PS (80:20:00) and PVdF:PMMA:PS (80:15:05) nanofibrous polymer electrolyte membranes at room temperature is shown in Fig. 7. The solution resistance indicates the pure resistance at high frequency that also relates to bulk resistance of the polymer electrolyte and the value of R_b locates in the left starting points in the Nyquist plots. The addition of amorphous PMMA cut down the crystallinity of PVdF promoted the lithium-ion mobility in the polymer electrolyte membrane. PS gives mechanical strength to the membrane and to some extent it also helps to lower the crystallinity of the PVdF. The calculated ionic conductivity value for PVdF: PMMA: PS (80:15:05) blend polymer electrolyte membrane is 2.50×10^{-2} s/cm.

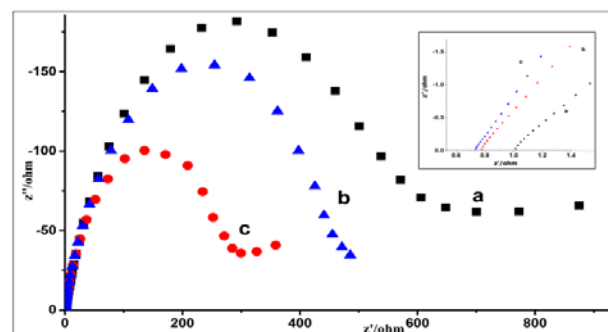


Figure 7 Nyquist plot of a) PVdF: PMMA: PS (100:00; 00) (b) PVdF: PMMA: PS (80:20:00) and (c) PVdF: PMMA: PS (80:15:05) nanofibrous membrane

The electrochemical performance of the cells is evaluated by galvanostatic cycling at room temperature under constant current of 0.1 C between 2.5 and 4.5 V. The initial cycle charge/discharge properties at a current density corresponding to 0.1 C-rate for PVdF: PMMA: PS (100:00:00), PVdF: PMMA: PS (80:20:00)

and PVdF: PMMA: PS (80:15:05) are 135 mAhg⁻¹, 147mAhg⁻¹ and 163 mAhg⁻¹ respectively. These results suggest that PVdF: PMMA: PS (80:15:05) nanofibrous polymer electrolyte membrane is a potential separator for lithium ion battery.

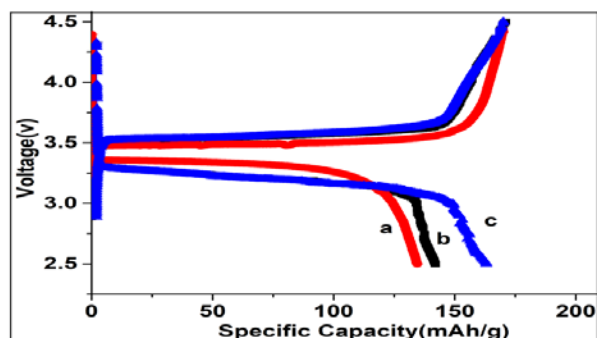


Figure 8 Battery performance of a) PVdF: PMMA: PS (100:00; 00) (b) PVdF: PMMA: PS (80:20:00) and (c) PVdF: PMMA: PS (80:15:05) nanofibrous membrane

1.4 Conclusions

PVdF: PMMA: PS blend fibers with diameter in nanoscale membranes were successfully prepared by electrospinning. PVdF: PMMA: PS blend membranes showed excellent electrochemical properties due to the interconnected porous structure. The addition of PMMA and PS enhances electrolyte uptake and ionic conductivity of PVdF: PMMA: PS blend membrane. PVdF: PMMA: PS (80:15:05) blend membranes shows excellent porosity, electrolyte uptake and ionic conductivity. These results show that PVdF: PMMA: PS (80:15:05) blend membranes nanofibrous polymer electrolyte membrane was found to be potential and promising separator for lithium ion batteries.

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