

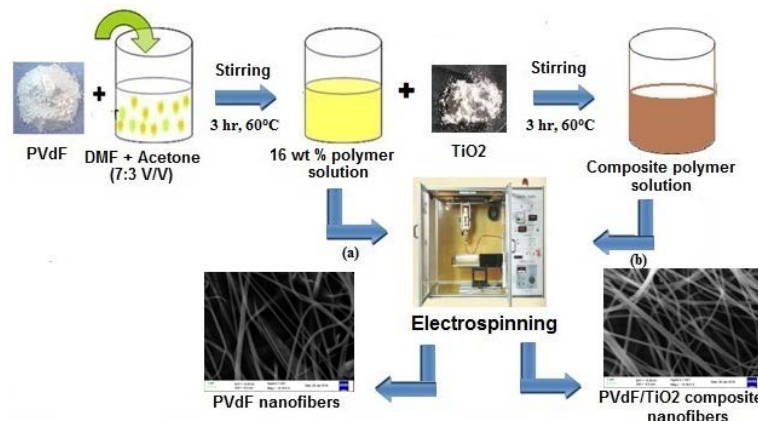
Titanium dioxide / poly(vinylidene fluoride) hybrid polymer composite nanofibers as potential separator for lithium ion battery

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ABSTRACT



Poly(vinylidene fluoride) / Titanium dioxide (PVdF/TiO₂) polymer composite nanofibers were fabricated by electrospinning. PVdF/TiO₂ composite nanofibers polymer electrolytes were prepared by soaking the composite nanofibers in 1 M LiPF₆ (lithium hexafluorophosphate) in ethylene carbonate : diethyl carbonate (EC:DEC) in 1:1 (v/v) ratio. PVdF/TiO₂ composite nanofibers exhibited high electrolyte uptake, high porosity and high ionic conductivity compared to that of pure PVdF. The higher electrochemical stability of PVdF/TiO₂ composite nanofibers polymer electrolyte as obtained from its linear sweep voltammetry compared to that of pure PVdF nanofibers polymer electrolyte. PVdF/TiO₂ composite nanofibers polymer electrolyte was found to be a good separator in lithium-ion battery applications.

Keywords: Polymer electrolyte, Electrospun nanofibers, Poly(vinylidene fluoride), Titanium dioxide nanoparticles, Lithium-ion battery

INTRODUCTION

Conventional rechargeable batteries usages are limited by their capacity and durability, but lithium ion rechargeable batteries have much greater capacity, durability having light weight and

are considered to be one of the most promising and practical rechargeable batteries. The development of rechargeable lithium-ion batteries (LIB) with high energy density, high-rate capability, and superior cycling performance is important for applications in automotive, military, electric vehicle and aerospace.¹ In a LIB, the separator plays an essential role in preventing the physical electronic contact between electrodes and serves as a liquid electrolyte reservoir to transport ions. Many efforts had been made to prepare potential separators using inorganic nanoparticles and organic polymers to improve the electrolyte wettability and uptake for LIB.² Currently, Micro-porous polyolefin is mainly used for preparation of separators for commercial lithium ion battery, which has relatively low porosity and poor wettability. Therefore,

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there is need to develop separator-cum electrolyte membrane to overcome these limitations. Polymer gel electrolytes are one of the most important classes of ion conducting polymeric materials having higher values of ionic conductivity as compared to that of liquid electrolytes. Polymer electrolytes with high porosity and wettability can be synthesized by different techniques such as solution casting, phase inversion, γ -ray irradiation method and electrospinning technique.³⁻⁶ Among them, electrospinning is very unique and useful technique to produce nanofibrous polymer electrolyte membrane. Electrospinning has rapidly achieved popularity as a simple and quick method for synthesizing nanofibers of polymers to achieve nanopores for improving conduction of lithium ions. Electrospinning of polymeric fibers draw a great attention on account of its versatility in spinning of polymeric fibers as well as its consistency in producing fibers in the nano-range with uniform morphology. These fibrous polymer membranes have ability to encapsulate electrolyte salt within the matrix because of its high porosity and an interconnected open pore structure. The most important advantages of the electrospinning technique are the liability to control the fiber diameters, high surface-to-volume ratio, high aspect ratio, and pore size as non-woven fabrics.^{7,8} Nowadays, many polymers are used for the synthesis of polymer electrolytes membrane such as poly(vinylidene fluoride) (PVdF), poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP), poly(methyl methacrylate) (PMMA), poly(acrylonitrile) (PAN) and poly(ethylene oxide) (PEO).^{9,10} PVdF is very favorable material because of its special properties like the high dielectric constant, strong chemical and electrochemical resistance. PVDF has a strong electron-withdrawing functional group (-C-F) and the high dielectric constant ($\epsilon = 8.4$), which is beneficial for larger dissolution of lithium salts and for a high concentration of charge carriers. But, the crystalline part of PVdF became hindrance to the migration of Li^+ ions, which may lead to lower charge/discharge capacities and low ionic conductivity.¹¹ In order to improve the ionic conductivity at room temperature, many efforts have been made to develop high conducting polymer electrolytes (PEs) by one of the best way to introduce other blending polymers like polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA) and thermoplastic polyurethane (TPU)^{12,13} or inorganic nanoparticles as fillers such as ZrO_2 , Al_2O_3 and SiO_2 into electrospun PVdF membranes for preparing composite polymer electrolytes.^{14,15} Fillers, such as MgAl_2O_4 and ZnAl_2O_4 added into PVDF-co-HFP or PVDF-HFP/PMMA polymer blends have recently been proposed as hybrid fibrous electrolyte nanocomposites.¹⁶⁻¹⁸ It has been reviewed that the hybrid composites polymer electrolytes are most suitable as separator for use in lithium ion batteries.

The TiO_2 was selected as nanofiller for PVdF polymer in the present investigation because of TiO_2 provides more electrolyte dissociation by the Lewis acid base interactions between the polar surface groups of TiO_2 and the electrolyte ionic species. Therefore, an organic/inorganic (PVdF/ TiO_2) hybrid composite nanofibers membrane was fabricated by electrospinning technique to prepare (PVdF/ TiO_2) hybrid composite nanofibers polymer electrolyte as a potential separator for lithium ion batteries. The effect of incorporation of TiO_2 nanoparticles on the properties of

the hybrid nanofibrous membrane and the polymer electrolyte for lithium ion batteries was investigated.

EXPERIMENTAL

Preparation of TiO_2 nanoparticles

In a typical process for the synthesis of TiO_2 nanoparticles, 3 ml titanium tetrachloride was slowly added drop wise into 30 ml of ethanol under constant stirring. The pH of the transparent yellowish solution was nearly 1.0-1.5 after adding all titanium tetrachloride. After stirring the mixture for 24 hr, sol was converted into gel and then it was dried under 120 °C for 1.5 h to evaporate water. Finally, dry-gel was calcined for 1 hr at 900 °C with ramping rate of 5 °C/min and rutile- TiO_2 nanoparticles were obtained.

Preparation of composite polymer electrolyte (CPE) membranes

In a typical process for the preparation of PVdF/ TiO_2 composite nanofibers, first the 12wt% of PVdF was dissolved in a mixture of dimethyl formamide (DMF) and acetone (7:3 V/V) in a beaker and then stirred for 3 hr at 60 °C until a homogeneous solution was formed. 4 wt% TiO_2 nanoparticles were added to PVdF polymer solution and stirred vigorously at room temperature until the complete dissolution of the solid reagents. The resulting homogeneous solution was degassed for 15 min to get the bubble free clear solution. The resultant viscous solution of PVdF/ TiO_2 was taken into 5 ml syringe and loaded in a syringe pump to form nanofibers by optimizing the electrospinning parameters such as solution feed rate 0.6 ml/hr, applied voltage between spinneret and collector 18 kV, distance between the tip of the spinneret and collector is 12.5 cm so as to produce highly porous, uniform diameter in nanoscale fibers.¹⁹ PVdF/ TiO_2 composite nanofibers were collected on aluminum foil wrapped on rotating collector which was grounded for proper aligning in one direction. In similar way, pure PVdF nanofibers were prepared without incorporation of TiO_2 nanoparticles in the PVdF polymer solution for comparison. The nanofibers were dried under vacuum pressure at 60°C for 24 hr. As-fabricated PVdF and PVdF/ TiO_2 composite nanofibers membrane were separately immersed in 1 M LiPF₆ in EC:DEC (1 : 1, v/v) solution for 60 minute at 30 °C in glove box for preparation of PVdF and PVdF/ TiO_2 composite nanofibers polymer electrolytes.

Characterizations

X-ray diffraction (XRD) of electrospun nanofibers membranes was carried on Rigaku D/MAX-RB X-ray diffractometer recorded using $\text{Cu-K}\alpha$ radiation with the scan rate 1°/min. Fourier transform infrared (FTIR) transmittance spectra of electrospun nanofibers membranes were recorded on α -Brucker model spectrophotometer in the range of 400–4000 cm^{-1} . The surface morphology and elemental composition of electrospun nanofibers membranes were investigated, using scanning electron microscope with EDX (Carl Zeiss EVO-18). The electrolyte uptake capacity of electrospun nanofibers membranes was determined by soaking the membranes in an electrolyte solution containing 1 M LiPF₆ in EC:DEC (1 : 1, v/v) and weighed it at regular intervals after removing the excess liquid electrolyte by wiping them.²⁰ Porosity % of electrospun nanofibrous membranes was determined by

immersing in n-butanol for 2 hr. The mass of nanofibrous membrane before and after immersion was measured.²¹ The ionic conductivity of polymer electrolytes was determined by measuring AC impedance at frequency range 1 mHz to 1 MHz and amplitude of 5mV using Zahner Zennium electrochemical analyzer. Polymer electrolyte membranes were sandwiched between two stainless steel blocking electrodes (SS/polymer electrolyte membrane/SS, SS: stainless steel) for the measurement of impedance. The electrochemical stability of polymer electrolyte membranes was studied by linear sweep voltammetry (Electrochemical workstation, Zehner Zennium). The measurement was carried out by using stainless steel (SS) as one electrode and lithium (Li) metal as another electrode between which polymer electrolyte membranes was sandwiched, at the scan rate of 1 mVs⁻¹ over the potential range of 2 – 6 V at room temperature.

RESULTS AND DISCUSSION

SEM images of TiO₂ nanoparticles, PVdF and PVdF/TiO₂ composite nanofibrous membranes are shown in Figure 1(a), 1(b) and 1(c) respectively. The shape of the TiO₂ nanoparticles is close to almost spherical morphology and consists of small grains distributed randomly in a range around 50 nm. It can be seen from SEM images of nanofibrous membranes that three dimensional web structures are observed by the interconnected ultrafine fibers for both the membranes. The interlaying of multi-fiber layers yield a porous structure between the fibers in the electrospun membrane, which is necessary to entrap and retain electrolyte effectively, and it helps an electrolyte to diffuse smoothly into the membrane. While comparing their SEM images, electrospun PVdF/TiO₂ composite membrane has a uniform nanofibrous morphology compared to that of pure PVdF membrane.

For two membranes, the electrospinning parameters which influence diameter of fibers, such as applied voltage, feeding speed of polymer solution and tip-collector distance were kept fixed. So it is obvious that introduction of TiO₂ caused an increase in viscosity of the polymer solution and led to uniform distribution of fibers with reduced nanoscale diameter.

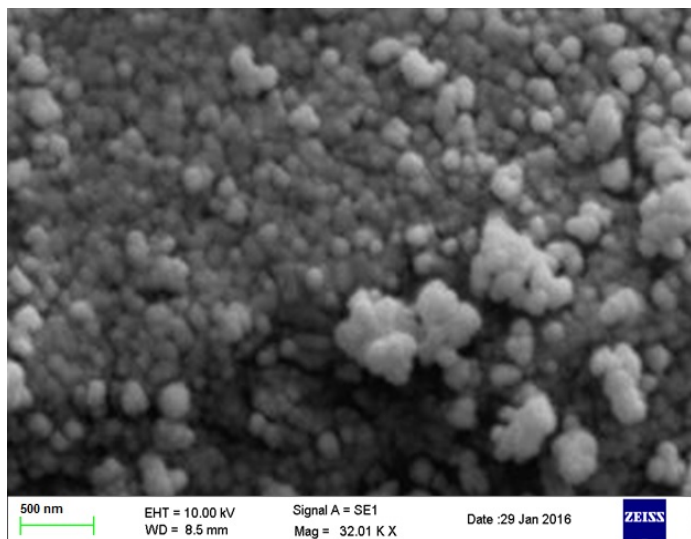


Figure 1(a): SEM image of TiO₂ nanoparticles

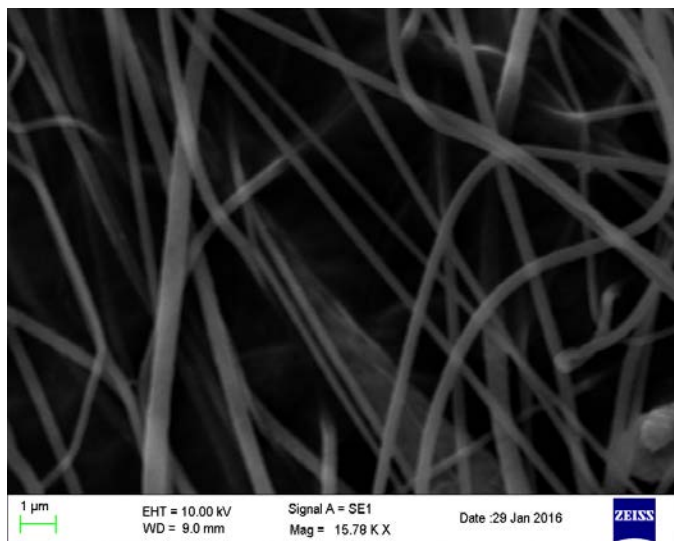


Figure 1(b): SEM image of electrospun PVdF nanofibers

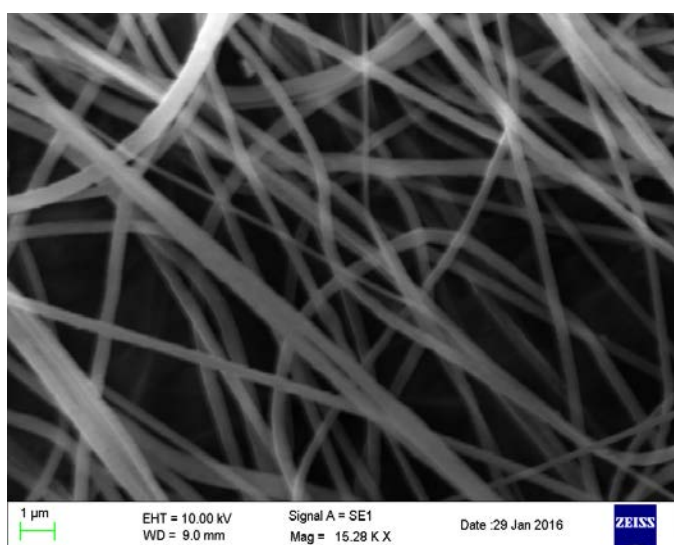


Figure 1(c): SEM image of electrospun PVdF/TiO₂ nanofibers

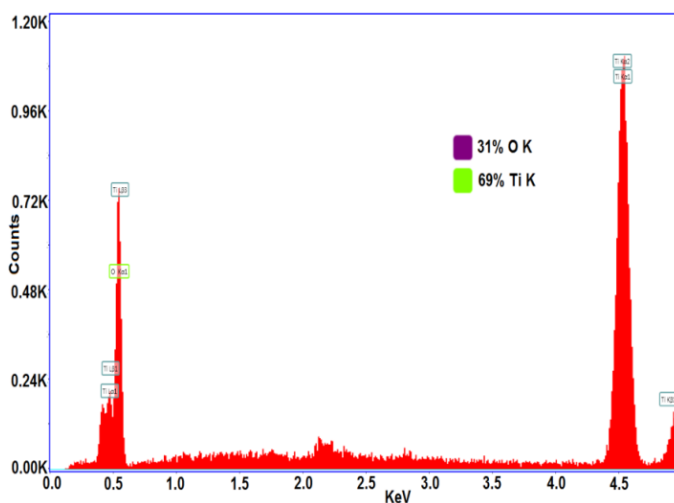


Figure 2(a): EDX spectrum of TiO₂ nanoparticles

Moreover, elemental mapping of TiO₂, pure PVdF nanofibers and PVdF/TiO₂ composite nanofibers membranes for carbon, fluorine, titanium, and oxygen, as shown in Figure 2(a), (b) and (c)

respectively, revealed the confirmation of TiO₂, pure PVdF and PVdF/TiO₂ composite formation.

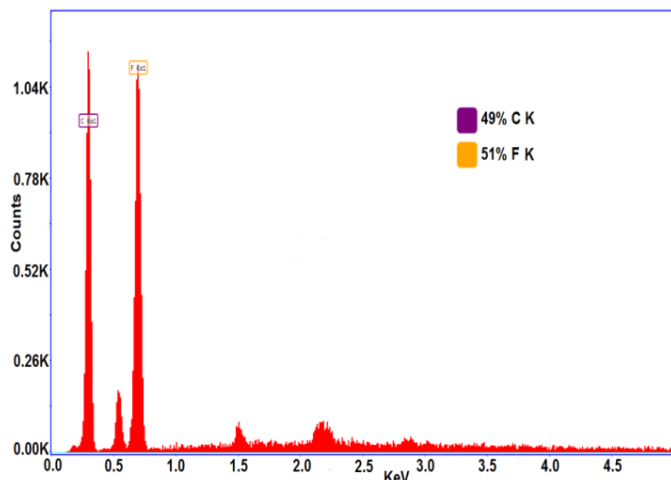


Figure 2(b): EDX spectrum of electrospun PVdF nanofibers

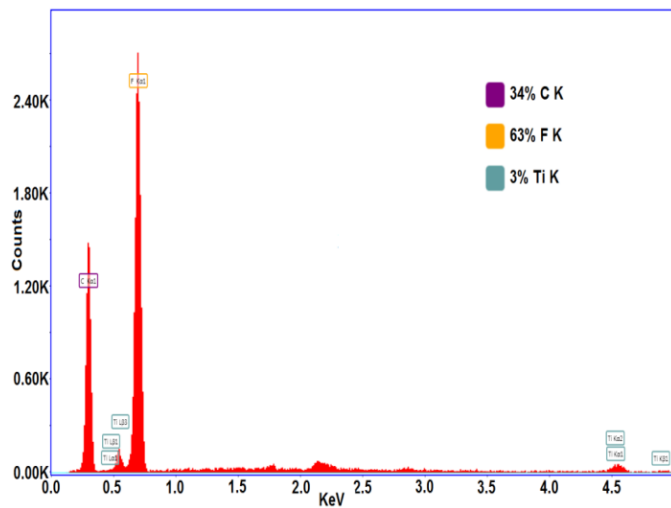


Figure 2(c): EDX spectrum of electrospun PVdF/TiO₂ nanofibers

XRD patterns of electrospun PVdF and PVdF/TiO₂ nanofibrous membranes along with TiO₂ nanoparticles are shown in Figure 3. It is apparent that the pure TiO₂ nanoparticles are crystalline and the positions of all the sharp peaks reveal that the TiO₂ is in rutile phase and having good agreement with reported data.²²⁻²⁴ Adopting the Scherrer formula, the calculated size of TiO₂ nanoparticles was found to be ~30 nm, consistent with the observed result from SEM image. From XRD patterns of electrospun PVdF membrane and PVdF/TiO₂ composite nanofibrous membrane, the presence of crystalline peaks and amorphous humps indicated the semi crystalline nature and it is well established that a very strong diffraction peak for PVdF membrane is observed at 2θ of 20°, which corresponds to 200 reflection of β-phase. Compared with electrospun PVdF membrane, electrospun PVdF/TiO₂ composite nanofibrous membrane showed a new diffraction peaks at 25° which corresponds to the peak of TiO₂. If the wt% of TiO₂ nanofiller increases, then crystallinity of the polymer has been reduced due to increase in the mobility of Li-ions through fine pore structures, which improved the ionic conductivity at room temperature. The

observed crystallinity of pure PVdF decreased with the addition TiO₂ fillers to 4 wt% and formation of amorphous phase of nanocomposite membranes take place. This indicates the successful introduction of TiO₂ into the electrospun PVdF membrane.

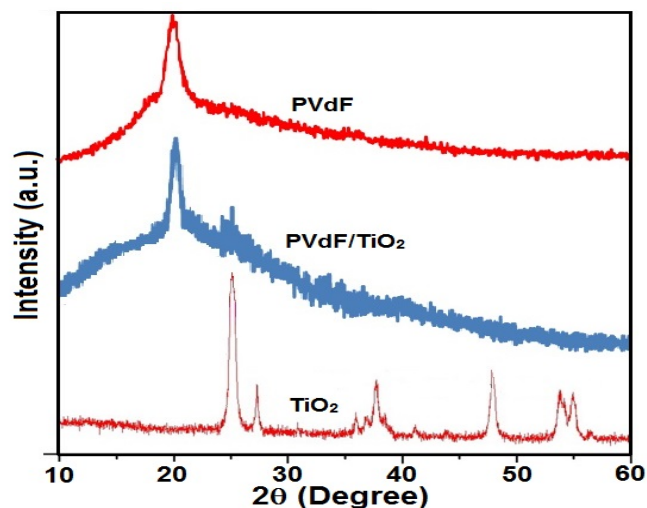


Figure 3: XRD patterns of TiO₂ nanoparticles, electrospun PVdF and PVdF/TiO₂ nanofibers

FTIR spectra of electrospun PVdF and PVdF/TiO₂ composite nanofibrous membranes are shown in Figure 4(a) and 4(b) respectively. The spectra reveal that both membranes mainly contain β-phase crystal structure of PVdF. For electrospun PVdF membrane, the peaks appearing at 612, 840, and 1275 cm⁻¹ are identified to the characteristic bands of β-phase for PVdF.²⁵ The 612 cm⁻¹ band is assigned to CF₂ bending vibration. The band at 840 cm⁻¹ is assigned to CH₂ rocking vibration.

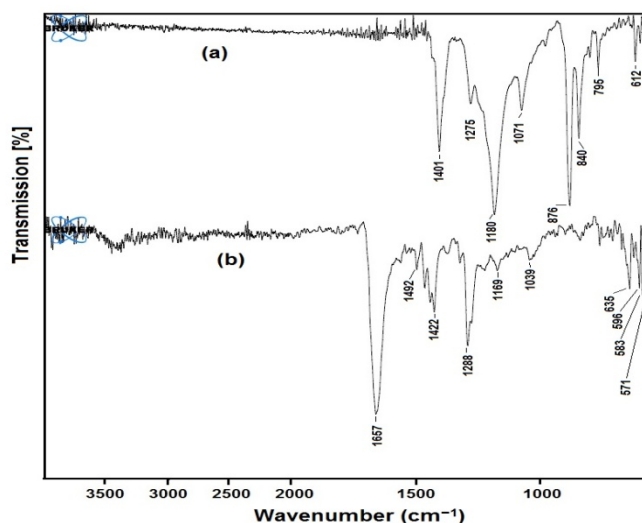


Figure 4: FTIR spectra of (a) PVdF and (b) PVdF/TiO₂ nanofibers

The band at 1275 cm⁻¹ is assigned to CF₂ asymmetric stretching vibration. These strong peaks are the evidence of the high content of β-phase. In the case of PVdF/TiO₂ composite nanofibrous membrane, the wider absorption peaks at 500-800 cm⁻¹ are due to the overlap of Ti-O-Ti stretching vibration of TiO₂ with the

absorption peaks.²⁶ It is also observed that the absorption peaks related to β -phase crystal structure of PVdF decrease in intensity by introducing the TiO_2 . These results indicate that the orientation of the PVdF chains was inhibited by the TiO_2 during the electrospinning process. The intensity of the absorption peaks of the PVdF membrane with fillers TiO_2 decreased due to interactions between nanoparticles and polymer chains suggesting that polarity of CF_2 groups decreases. The appearance of new peaks in the composite PVdF- TiO_2 nanofibrous membrane, confirms the miscibility of TiO_2 with PVdF.

The thermal stability of PVdF and hybrid PVdF/ TiO_2 nanofibrous membranes was studied by TGA measurement. Figure 5 shows TGA plots for pure PVdF membrane and the hybrid PVdF/ TiO_2 nanofibrous membrane. It can be seen from the figure that both the membranes are thermally stable upto 400°C and then degradation of the membranes starts. There is weight loss for pure PVdF starting at 410 °C and PVdF/ TiO_2 starting from 450 °C. While comparing the thermal stability of nanofibrous membrane under study, PVdF/ TiO_2 was found to be more thermally stable due to nanoparticles of TiO_2 in the composite. The stability of PVdF improves after doping by TiO_2 .

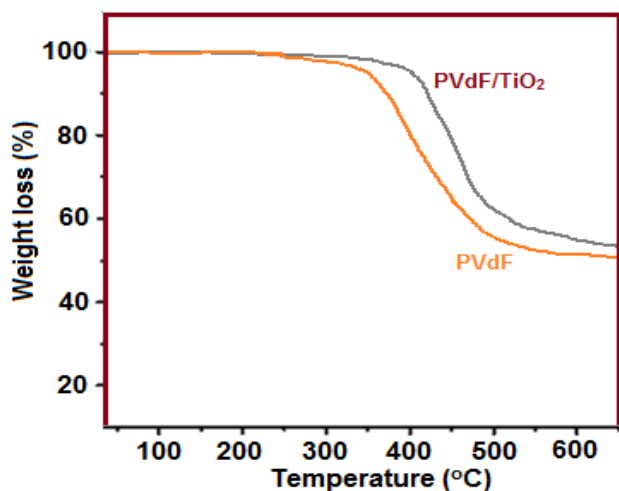


Figure 5: TGA curves of PVdF and PVdF/ TiO_2 nanofibers

The ionic conductivity of the pure PVdF and PVdF- TiO_2 nanofibrous membrane electrolyte was determined at room temperature by AC impedance spectroscopy. Figure 6 shows typical AC impedance spectra of pure PVdF and PVdF- TiO_2 nanofibrous membrane electrolyte. The intercept of inclined spike on the real axis represents the bulk resistance (R_b) of all of the electrolyte membranes. The bulk resistance (R_b) of PVdF and PVdF- TiO_2 at 30°C was found to be 0.8 and 0.6 ohm respectively as clearly seen from inset of Figure 6. The ionic conductivity of electrospun membrane was calculated from the analyzed impedance data and sample dimensions. The ionic conductivity of pure PVdF was found to be $3.517 \times 10^{-3} \text{ S cm}^{-1}$ which increased with relative content of TiO_2 for PVdF- TiO_2 nanofibrous membrane to about $4.15 \times 10^{-3} \text{ S cm}^{-1}$.²⁷ PVdF nanofibrous polymer electrolytes are generally thought to comprise a solid fibrous phase, an amorphous swollen fibrous phase, and a liquid phase with the electrolyte solution in its pores.²⁸ Because the high crystalline content of PVdF prevents the migration of lithium ions,

ion conduction mainly depends on the entrapped liquid phase in the pore structure. The high ionic conductivity can be mainly ascribed to the unique porous structure of the electrospun membranes. Furthermore, amorphous swollen phase takes a tight hold of electrolyte solution and prevents the leakage of solution. This also influences the ionic conductivity of the polymer electrolytes partially.²⁹ The increase of ionic conductivity by incorporation of TiO_2 is due to the increase of the liquid electrolyte uptake and the amorphous phase content, which contributes to the formation of more tunnels allowing greater Li ion migration.

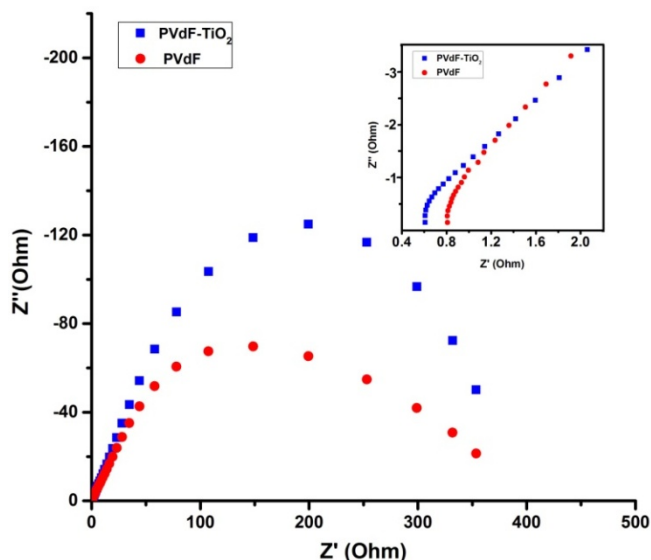


Figure 6: AC impedance spectra of PVdF and PVdF/ TiO_2 nanofibers electrolytes

Porosity is one of the important parameters of the polymer electrolyte membranes. The interlaying of the fibers generates porous structure in the electrospun membrane. The n-butanol does not involve directly with the membrane it rather entered the pores and occupies all the available pores, and thus gives a measure of the total pore volume in the material. The porosity % of PVdF/ TiO_2 composite nanofibrous membrane was found to be 86% compared to 72% to that of pure PVdF. The high porosity can be used to explain the high electrolyte uptake of PVdF/ TiO_2 composite nanofibrous membrane. The pores in membrane are interconnected with each other, which is beneficial for conduction of ion in lithium ion battery. Figure 7 represents the electrolyte uptake behavior of the electrospun pure PVdF and PVdF/ TiO_2 nanofibrous membrane electrolyte. The requirement of good lithium ion battery separator is that the separator should be completely and very quickly wetted out in the typical liquid electrolyte. Poor compatibility between the electrolyte and the porous film separator can lead to poor long-term stability of the battery, so for avoiding this issue it is important to fast liquid penetration into the membranes to form the polymer electrolyte. The higher electrolyte uptake can make an improvement of ionic conductivity.

Both membranes exhibit a high electrolyte uptake. Electrospun PVdF membrane showed an electrolyte uptake of 270% after 60 min. For electrospun PVdF/ TiO_2 composite nanofibrous

membrane, the uptake electrolyte is up to 370% after 60 min. The improved uptake capability is mainly due to the excellent affinity of TiO₂ with carbonate-based liquid electrolyte and the increase of amorphous phase of PVdF.³⁰ A higher uptake of the liquid electrolyte means the existence of more Li⁺ in the same volume, which leads to the high ionic conductivity of the composite polymer electrolyte. It is a very important function for polymer electrolytes to prevent the leakage of electrolyte solution and ensure the stable properties of lithium batteries.

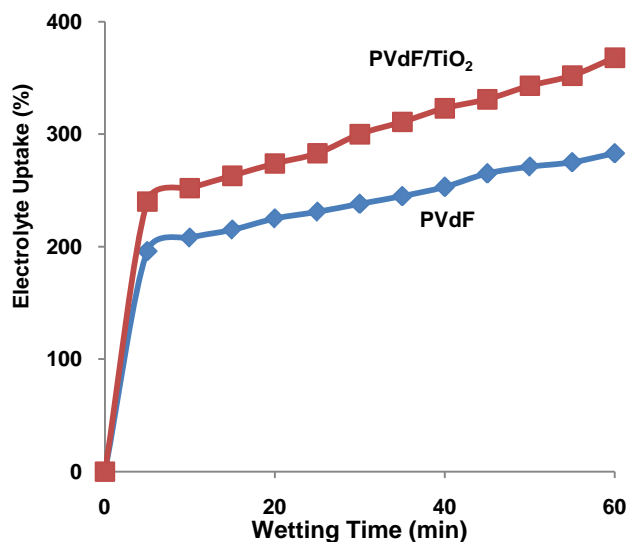


Figure 7: Electrolyte uptake of PVdF and PVdF/TiO₂ nanofibers

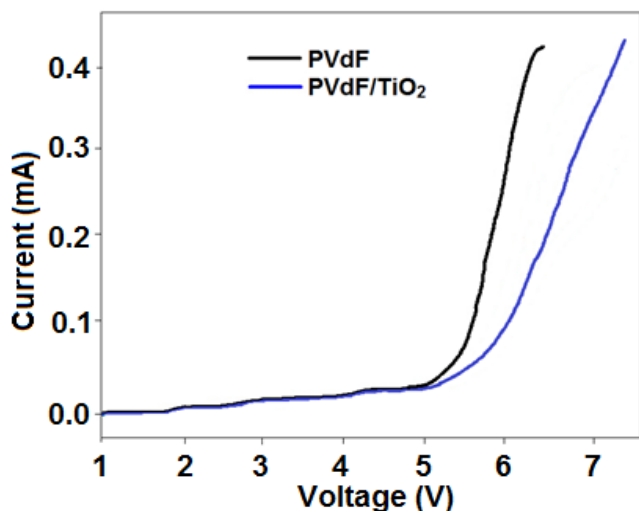


Figure 8: Linear sweep voltammogram curves of PVdF and PVdF/TiO₂ composite nanofibrous polymer electrolytes

The results of electrochemical stability tests of the polymer electrolytes by linear sweep voltammetry are shown in Figure 8. In this work, both PVdF fibrous polymer electrolyte and PVdF/TiO₂ composite fibrous polymer electrolytes exhibited good electrochemical stability. The onset voltage of current increase for PVdF fibrous polymer electrolyte is around 5.0 V. With the incorporation of the TiO₂ into the polymer matrix, the voltage value for the onset of current increase is further increased up to 5.2 V, which is stable enough to endure the high voltage of

cathode materials in the LIBs. The higher electrochemical stability of PVdF/TiO₂ composite fibrous polymer electrolyte than that of PVdF fibrous polymer electrolyte may be due to the hybrid combination of PVdF and TiO₂. Due to the excellent affinity for TiO₂, the electrolyte solution is more tightly trapped in the pores of the membrane in the composite membrane. These results suggested that the prepared PVdF/TiO₂ composite fibrous polymer electrolytes are expected to be suitable for application in lithium-ion batteries.

CONCLUSIONS

Hybrid nanocomposite nanofibrous polymer electrolyte membranes were successfully prepared by electrospinning method. SEM micrographs showed that polymer electrolyte membranes with diameter of fibers in nanoscale. The ionic conductivity, high porosity with smaller average fiber diameter and electrolyte uptake were found to be enhanced after the addition of TiO₂ nanofiller. PVdF-TiO₂ composite nanofibrous membranes prepared via electrospinning is very much suitable as the polymer electrolyte for polymer lithium-ion batteries.

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