

Preparation of PVDF/SiO₂ Composite Nanofiber Membrane Using Electrospinning for Polymer Electrolyte Analysis

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ABSTRACT

Superhydrophobic poly(vinylidene fluoride) PVDF-SiO₂ composite membranes with different % of SiO₂ contents were prepared by electrospinning. The surface morphologies of the membranes are characterized by using scanning electron microscopy. The nanofibers in the membranes were stacked in layers to produce fully interconnected pores that resulted in high porosity. The incorporation of SiO₂ into the nanofiber membrane improved the ionic conductivity from $0.2428 \times 10^{-4} \text{ Scm}^{-1}$ to $7.731 \times 10^{-4} \text{ Scm}^{-1}$ at room temperature. The surface roughness of the membranes increased with increasing the SiO₂ content, while the average diameter of nanofibers was rarely affected. Superhydrophobic PVDF membrane with a contact angle larger than 136° was prepared by the electrospinning of the SiO₂ functionalized PVDF. The surface composition of the membranes is analyzed by using FTIR and the contact angles and water drops on the surface of the membrane are measured. The contact angle experimental results of PVDF-SiO₂ composite membranes showed an improvement of hydrophobicity with % of nano SiO₂.

Keywords: Electrospinning Poly(vinylidene fluoride); Silica Nanoparticle; Nanofiber Membrane; Superhydrophobicity

1. Introduction

Polymer electrolytes have attracted great interest compared to traditional liquid electrolytes, which provide the advantages to develop lighter and safer batteries with long shelf life, leak proof construction and easy fabrication into desired shape and size [1]. There have been many efforts to develop polymer electrolytes with good ambient temperature conductivity and stable electrode/electrolyte interfacial properties with minimum resistance to ion transportation [2,3]. The properties of porous host polymer membrane such as pore size, porosity and pore size distribution are strongly dependent on its processing methods. Different methods such as solvent casting, plasticizer extraction and phase inversion have been adopted for the preparation of porous polymer membranes [4-6]. However, polymer membranes made by these methods show low-rate capabilities at high discharge rates because of low-order pore size, low porosity and poor channel in ionic conduction.

Electrospinning is an emerging technique to prepare polymer membranes that are composed of ultrafine fibers with micron and sub-micron diameter. Electrospinning is a process for producing superfine fibrous and porous membranes by forcing a polymer melt or solution through a spinneret with an electric field. The average diameter of the fibers produced by electrospinning is at least 10 - 100 times smaller than the conventional fibers produced by melt spinning [7]. In the electrospinning process, a high electric power is in the range of kilovolts applied to overcome the surface tension of the polymer drops. The applied voltage pulls charges from inside onto the surface of the drop. The molecules in the surface of the drops repel each other and facilitate fresh molecules to reach onto the surface of the drops. Under the right choice of conditions, the drop can become a rapidly growing polymer jet that can follow a tightly looping spiral path. The jet's width shrinks to as little as few nanometers and its length increases to few micrometers during the process [8].

Electrospun polymer membranes from polymers such

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as poly(vinylidene fluoride) (PVDF), poly(vinylidene fluoride-cohexafluoropropylene) (PVDF-HFP) and polyacrylonitrile (PAN) are particularly suitable as host matrices for polymer electrolytes [9-11]. The interlaying of thin fibers generates high porosity of over 80% with fully interconnected pore structure and very large surface area-to-volume ratio facilitating high electrolyte uptake and easy transport of ions. Moreover, the resulting polymer electrolyte showed lower bulk impedance and higher rate capability [10].

Inorganic nanoparticles like ZrO₂, Al₂O₃, TiO₂ and SiO₂ have been used for preparing composite polymer electrolytes [10-12]. These inorganic nanoparticles improve the ionic conductivity of polymer electrolytes by reducing the crystallinity of the host polymer and introduce Lewis acid-base interaction between the polar groups of the inorganic nanoparticles and the electrolyte ionic species [13]. Moreover, inorganic nanoparticles enhance the mechanical properties of polymer electrolytes and the interfacial stability between polymer electrolyte and lithium electrode [14]. Among them, SiO₂ has been known as an attractive material for preparing composite polymer electrolytes because it supports the ionic mobility by its starburst shape which effectively influences the order packing tendency of the host polymer chains [15].

PVDF has become a favorable polymer matrix for porous polymer electrolytes due to its appealing properties such as high dielectric constant and strong electron-withdrawing functional groups (-C-F) [16,17]. In the PVDF based porous polymer electrolytes, the absorbed liquid electrolyte is responsible for the ionic conduction while the PVDF matrix acts as the supporting backbone that separates the electrodes. However, mechanical strength is often sacrificed to obtain sufficient conductivity for commercial usage when the amount of liquid electrolyte is increased [18]. Nevertheless, the leakage of electrolyte solution remains due to a phase separation between the polymer matrix and the absorbed electrolyte solution. The loss of electrolyte solution may also lead to a failing of the electrode/electrolyte contact as well as a reduction of ionic conductivity [19]. Therefore, it is of great importance to search for novel safe polymer electrolytes to create a new generation of high performance lithium batteries.

In recent years, electrospinning technology is used for the preparation of highly porous membranes that ideally suits for the application as polymer electrolytes/separators in lithium batteries [20,21]. Several electrospun membranes based on P(VdF-HFP) were reported [22-25]. These membranes showed ionic conductivity in the order of mScm⁻¹ at room temperature and were electrochemically stable at potentials higher than 4.5 V versus Li/Li⁺. Recently, nanosize SiO₂ particles were incorporated into

P(VdF-HFP) membrane during electrospinning [26]. An ionic conductivity of 7.731×10^{-4} Scm⁻¹ was achieved. In the present study, an attempt was made to develop a new type of organic-inorganic composite nanofiber membranes based on PVDF-SiO₂ via electrospinning method. The SiO₂-dispersed PVDF nanofiber membranes led to excellent morphology suitable for the enhancement of electrochemical performance by providing large surface area, good electrolyte uptake, high contact angle and high ionic conductivity.

2. Experimental Details

2.1. Preparation of Electrospun Nanofiber Membranes

Poly(vinylidene fluoride) (PVDF), fumed silica (SiO₂), N,N-dimethylformamide (DMF), lithium hexafluorophosphate (LiPF₆), ethylene carbonate (EC) and dimethyl carbonate (DMC) were purchased from Sigma-Aldrich Co. and used without further purification. For SiO₂, the particle size is 70 nm and the surface area is about 390 m²·g⁻¹. Other reagents and solvents were commercially purchased and used as received.

The electrospinning setup utilized in this study consisted of a syringe and needle (ID = 0.4 mm), a ground electrode and a high voltage supply (ZEONICS SYSTEMS HIGH VOLTAGE D.C. P/S). The needle was connected to the high voltage supply, which could generate positive DC voltages up to 40 kV. For the electrospinning of PVDF-SiO₂ composite nanofiber membranes, PVDF was first dissolved in DMF at a concentration of 18 w/v% and then SiO₂ was mixed with different concentration under 60°C for 12 hours. The contents of SiO₂ in the composite solutions were 0, 0.3%, 0.5%, and 0.7 wt% based on the weight of PVDF. The composite solution held in a 5 ml syringe was delivered into a needle spinneret by a syringe pump (KDS 100, KD Scientific Inc.) with a mass flow rate of 1.5 ml·h⁻¹. The steel needle was connected to an electrode of a high voltage supply and a grounded Aluminium foil was placed at 15 cm distance from the needle tip to collect the nanofiber membranes. The positive voltage applied to the composite solutions was 18 kV. All the experiments were carried out at room temperature and below 60% RH. After the electrospinning, the nanofiber membranes were carefully peeled off from the Aluminium foil and put into oven under 40°C for 12 hours.

2.2. Characterization Techniques

The morphology of the electrospun PVDF-SiO₂ membrane was observed using scanning electron microscopy (studied by computer controlled Hitachi S3000 H SEM) under vacuum condition. The sample was sputtered with thin film of gold prior to the SEM measurement.

FTIR spectra of the samples were obtained with a PE IR SPECTRUM ASCII PEDS 1.60 in the wavenumber range 400 - 4000 cm⁻¹. The electrospun membrane was soaked in 1 M LiPF₆ in EC/DMC (1:1, v/v). An ionic conductivity cell was assembled by sandwiching a given polymer electrolyte between two stainless steel (SS) blocking electrode (1 × 1 cm). The ionic conductivities were measured by the impedance method of the SS/polymer electrolyte/SS at room temperature, using Ecochemie-Potentiostat/Galvanostat for impedance studies (Model: Autolab PGSTAT 30, The Netherlands) over the frequency range of 100 mHz to 2 MHz. The electrolyte resistance R was measured using a FRA (Autolab PGSTAT 30, Netherlands) with a 1260 frequency response analyzer controlled by a computer. The ac oscillation was 10 mV. The data were analyzed by Z-plot software. The ionic conductivity of the membrane σ was then calculated by the equation $\sigma = l/RA$, where l is the thickness of the film, R is the resistance electrolyte and A is the area of the film. The wettability of thin film of PVDF-SiO₂ composites (0.3%, 0.5%, and 0.7%) were determined by contact angle measurement using VCA optima, ACT product, INC. Hydrophilic or Hydrophobic characteristic nature of samples were estimated by contact angle (θ) value. The wetting liquid was Millipore-grade distilled water (liquid surface tension (γ) = 72.8 mJ·m⁻²) [27]. 5 μ l of water was added uniformly over the surface of the membrane. Contact angle was measured after 1 minute of water addition to provide the configuration between the measurements. When a drop of liquid is brought into contact with a flat solid surface, the final shape taken by the drop is expressed by " θ ". The increased value of $\cos\theta$ denoted higher wettability characteristics of a material.

3. Results and Discussion

3.1. PVDF-SiO₂ Membrane Preparation and Their Morphological Studies

The electrospinning was performed with 18 w/v% poly(vinylidene fluoride) (PVDF) solution in order to obtain nanofiber membranes that consist of bead-free fibers with uniform size and well-defined morphology. In the electrospinning of the polymer solution, the molecular chain entanglements prevent the breakup of the electrically driven jet into individual droplets, so that electrostatic stresses allow the jet to elongate and be deposited as ultrafine nanofiber membranes on the collector. PVDF-SiO₂ composite nanofiber membranes were prepared by electrospinning from PVDF-SiO₂ solutions with different % of SiO₂ contents. The % of SiO₂ in the mixed solutions were 0 (PVDF), 0.3 wt% (SiO₂—0.3 wt%), 0.5 wt% (SiO₂—0.5 wt%) and 0.7 wt% (SiO₂—0.7 wt%) based on the weight of PVDF used.

The surface morphology of electrospun composite nanofiber membranes are shown in **Figure 1**. The nanofiber membranes exhibited a fully interconnected membrane with nanosize distribution. The surface roughness increased with increasing the SiO₂ content, while the average diameter of nanofibers was rarely affected. Due to confirming strong peak from FTIR and surface roughness through the SEM that SiO₂ presents in the polymer matrix.

3.2. FTIR Studies

FTIR analysis was carried out in the range of 400 - 4000 cm⁻¹ to understand and confirm the presence of functional groups in the PVDF-SiO₂ nanofiber membranes. As shown in **Figure 2** three strong peaks are observed at the range of 1392, 854 and 1178 cm⁻¹. The former two peaks were assigned due to the C-F stretching vibration and the latter one peak was assigned due to the C-C bond of the PVDF. In the case of the composite nanofiber membrane, the peak observed at 478 cm⁻¹ may be associated with Si-O-Si stretching vibration of SiO₂.

3.3. Conductivity Studies

The ionic conductivities of the nanofiber membranes were calculated at room temperature by the impedance method. **Figure 3** shows the impedance data of polymer electrolytes based on electrospun nanofiber membranes with or without SiO₂. The impedance responses are typical of electrolytes with a major part towards total resistance from bulk resistance and only a minor contribution from grain boundary resistance. The real-axis representing the electrolyte/electrode double layer capacitance was obtained for all samples over the whole range of frequency evaluated. The intercept on the real-axis exhibiting bulk resistance varies between 0.242 Ω and 7.731 Ω , which reduces with increasing the SiO₂ content in the nanofiber membranes.

From the impedance data, the ionic conductivities of the nanofiber membranes at room temperature were calculated and presented in **Figure 4**. The ionic conductivity largely depends on the pore structure that entraps liquid electrolytes and hence the formation of pores in membranes is very important for obtaining proper channel of ionic conduction [28]. The ionic conductivities of all samples were higher than 0.242×10^{-4} Scm⁻¹ because of interwoven structure introduced during electrospinning. In addition, the incorporation of SiO₂ into the nanofiber membrane improved the ionic conductivity from 0.242×10^{-4} Scm⁻¹ to 7.731×10^{-4} Scm⁻¹.

3.4. Electrolyte Uptake

At presents a relationship of the electrolyte uptake of the nanofiber membranes. The data was obtained by soaking

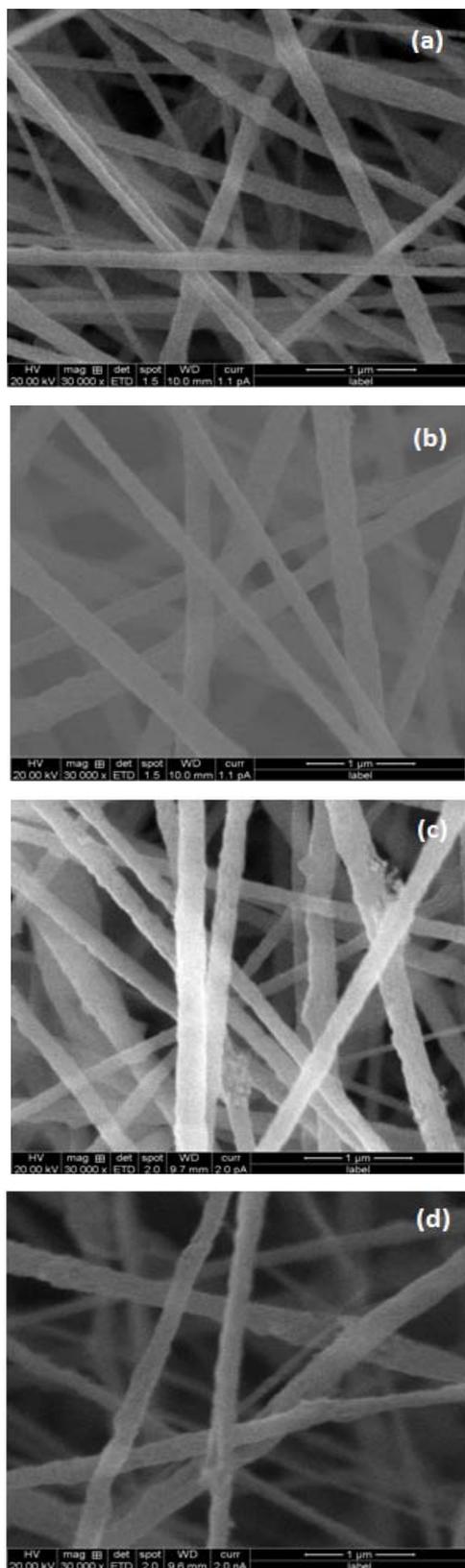


Figure 1. SEM images of electrospun composite nanofiber membranes with different SiO₂ contents: (a) Pure PVDF; (b) SiO₂ 0.3 wt%; (c) SiO₂ 0.5 wt%; (d) SiO₂ 0.7 wt%.

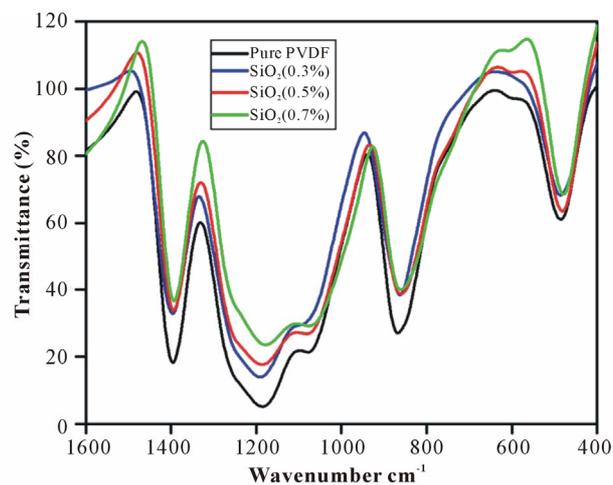


Figure 2. FTIR Spectra of 1) Pure PVDF; 2) SiO₂ 0.3 wt%, 3) SiO₂ 0.5 wt%; 4) SiO₂ 0.7 wt% .

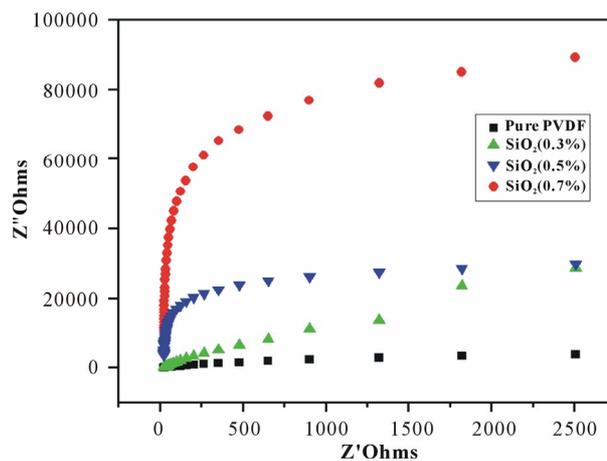


Figure 3. Impedance spectra of polymer electrolyte based on the nanofiber membranes with different SiO₂ contents 1) Pure PVDF; 2) SiO₂ 0.3wt%; 3) SiO₂ 0.5 wt%; 4) SiO₂ 0.7 wt% .

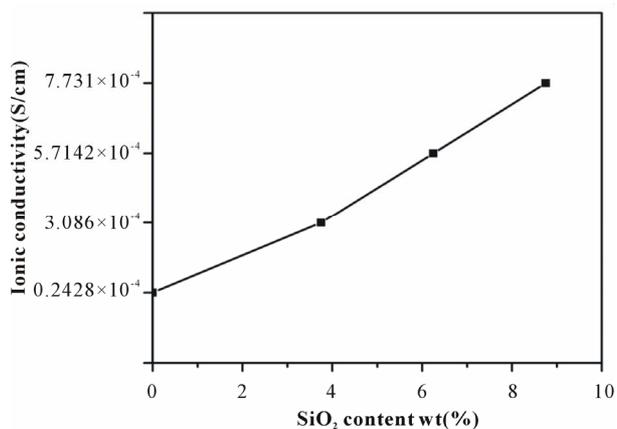


Figure 4. Variations of ionic conductivity in the nanofiber membranes with different SiO₂ contents.

the nanofiber membranes in the liquid electrolyte of 1 M LiPF₆ for a period of 1 h. The electrolyte uptake is observed to increase steadily with the SiO₂. In the case of SiO₂ 0.7 wt% membrane, the electrolyte uptake reached to ~450%.

The high retention ability and faster penetration of liquid electrolyte into the fibrous membranes are due to the unique pores generated from the interconnected fibers. So that pores and voids are increases the ionic conductivity also increases. Hence the uptake process is stabilized within the initial 10 min. PVDF-SiO₂ membrane (0.7 wt%) showed the highest value ~450%, because of its uniform fiber diameter and high specific surface area. As shown in **Figure 5**.

3.5. Wettability Test

Contact angles are commonly specified in degrees, the test fluid used in the measurements must be stated, for its surface tension will affect the angle (Young's equation). Contact angles are used to predict wettability and adhesion, and to indicate monolayer overage of adsorbed or deposited films. Another use of contact angles is to estimate "surface free energy" by using such theories as the Girifalco, Owens-Wendt, Wu, or Lewis Acid/Base models.

Although contact angles of upto 127.10°, 133.33°, 134.80° and 136.50° can be reached by directly electrospinning PVDF and SiO₂ composite solutions, respectively. Therefore, PVDF and SiO₂ composite were used to successfully prepare superhydrophobic membranes with high contact angles of 134.80° and 136.50° respectively. Membranes prepared by electrospinning method have much higher contact angle than because of the high surface area of the formed fibers that ranges from nanometer to submicron scale. As shown in **Figure 6**.

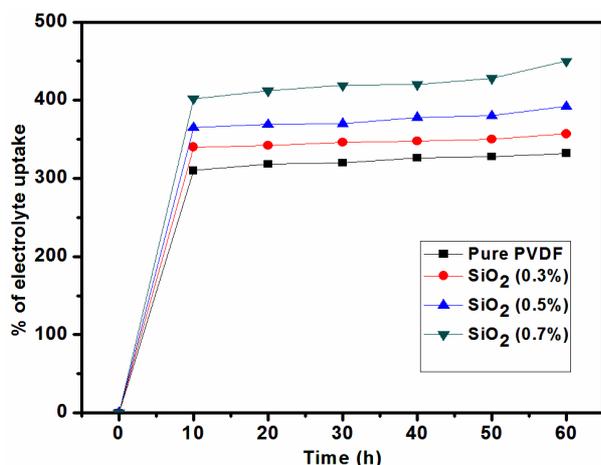


Figure 5. Electrolyte uptake of the nanofiber membrane with different SiO₂ contents.

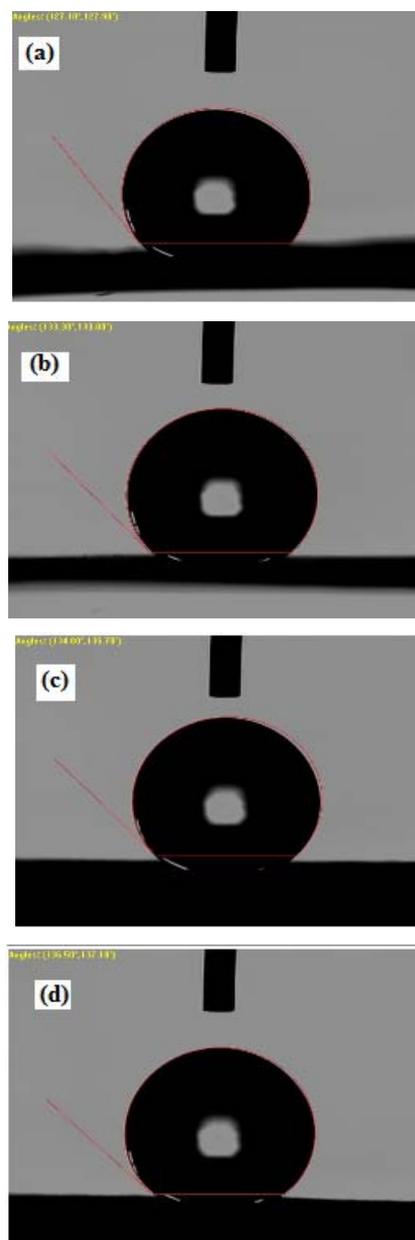


Figure 6. Contact angle measurement on (a) Pure PVDF; (b) SiO₂ 0.3wt%; (c) SiO₂ 0.5 wt%; (d) SiO₂ 0.7 wt%.

4. Conclusion

In the present study, organic-inorganic composite nanofiber membranes were prepared by electrospinning of PVDF solutions with different nano SiO₂ content, which showed a porous morphology formed by interlaying of the fibers. The presence of the SiO₂ nanoparticles improved the conductivity and wettability of the nanofiber membranes. The introduction of nano SiO₂ created amorphous regions by the way of the interactions between the SiO₂ surfaces and the polymer chains. The ionic conductivity of the membranes increased with in-

creasing the SiO₂ content at different concentration. The electrolyte uptake reached to ~450%. The high retention ability and faster penetration of liquid electrolyte into the fibrous membranes are due to the unique pores generated from the interconnected fibers. It was observed that both PVDF and SiO₂ composite membranes can only reach contact angles lower than 127.10° by either coupling or by electrospinning pure PVDF and SiO₂ composite solutions. A superhydrophobic membrane with contact angles of 136.50° was achieved by electrospun PVDF-SiO₂ composite nanofiber membrane. It is concluded that the composite nanofiber membranes fabricated by electrospinning offer a new approach for application in high-performance lithium batteries. Superhydrophobic PVDF membranes were prepared by electrospinning of fumed silica functionalized PVDF.

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