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Characteristics of electrospun PVDF/SiO_2 composite nanofiber membranes as polymer electrolyte

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ABSTRACT

Composite nanofiber membranes were prepared by electrospinning from poly(vinylidene fluoride) (PVDF)–SiO_2 blend solutions with different SiO_2 contents. The nanofibers in the membranes were stacked in layers to produce fully interconnected pores that resulted in high porosity. The surface roughness of the membranes increased with increasing the SiO_2 content, while the average diameter of nanofibers was rarely affected. The mechanical properties of the nanofiber membranes were significantly improved by the use of SiO_2. XRD results revealed that electrospun nanofiber membranes contained mainly β-phase crystal structure of PVDF. The crystallinity obtained from the DSC data reduced with the increase of the SiO_2 content from 44.9% to 37.1% due to the inhibited crystallization of the polymer by the inorganic particles during the solidification process. These nanofiber membranes exhibited a high electrolyte uptake, which reached to ~500%. Moreover, the incorporation of SiO_2 into the nanofiber membrane improved the ionic conductivity from 1.7×10^{-3} S cm^{-1} to 4.7×10^{-3} S cm^{-1} at room temperature.

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.

Recently, many researchers have tried to employ the electrospinning technique to prepare polymer membranes that are composed of ultrafine fibers with micron and sub-micron diameters. Electrospun polymer membranes from polymers such as poly(vinylidene fluoride) (PVDF), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and polyacrylonitrile (PAN) are particularly suitable as host matrices for polymer electrolytes [7–9]. 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 electrolytes showed lower bulk impedance and higher rate capability [8].

PVDF has become a favorable polymer matrix for porous polymer electrolytes due to its appealing properties such as high dielectric constant and strongly electrowithdrawing functional groups (–C–F) [10,11]. 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 [12]. 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. Therefore, it is of great importance to search for novel safe polymer electrolytes to create a new generation of high performance lithium batteries.

Inorganic nanoparticles like ZrO_2, Al_2O_3, TiO_2 and SiO_2 have been used for preparing composite polymer electrolytes [8,9,13].

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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 [14]. Moreover, inorganic nanoparticles enhance the mechanical properties of polymer electrolytes and the interfacial stability between polymer electrolyte and lithium electrode [15]. Among them, SiO_2 has been known as an attractive material for preparing composite polymer electrolytes because it supports the ionic mobility by its starburst shape which effectively disturbs the order packing tendency of the host polymer chains [16].

In the present study, an attempt was made to develop a new type of organic–inorganic composite nanofiber membranes based on PVDF–SiO_2 via electrospinning method. The objective of this work was to systematically examine the morphology, porosity, mechanical properties as well as electrochemical properties of nanofiber membranes with different content of SiO_2. The SiO_2-dispersed PVDF nanofiber membranes led to excellent morphology suitable for the enhancement of electrochemical performance by providing large surface area, high porosity and high ionic conductivity.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride) (PVDF), fumed silica (SiO_2), *N*,*N*-dimethylformamide (DMF), lithium hexafluorophosphate ($LiPF_6$), ethylene carbonate (EC) and dimethyl carbonate (DMC) were purchased from Sigma–Aldrich Co. and used without further purification. For SiO_2, the particle size is 70 nm and the surface area is about 390 $m^2\ g^{-1}$. Other reagents and solvents were commercially available and were used as received.

2.2. Preparation of electrospun nanofiber membranes

The electrospinning setup utilized in this study consisted of a syringe and needle (ID = 0.41 mm), a ground electrode, and a high voltage supply (Chungpa EMT Co.). The needle was connected to the high voltage supply, which could generate positive DC voltages up to 40 kV. For the electrospinning of PVDF–SiO_2 composite nanofiber membranes, PVDF was first dissolved in DMF at a concentration of 18 w/v% and then SiO_2 was mixed with different concentration under 60 °C for 12 h. The contents of SiO_2 in the composite solutions were 0, 3, 5, and 7 wt% based on the weight of PVDF. The composite solution held in a 10 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 stainless steel plate 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 experiments were carried out at room temperature and below 60% RH. After the electrospinning, the nanofiber membranes were carefully peeled off from the stainless steel plate and put into oven under 40 °C for 12 h.

2.3. Characterization of nanofiber membranes

The morphology of electrospun nanofiber membranes was observed by a field emission-scanning electronic microscope (FE-SEM, S-4800, Hitachi). Prior to SEM observation, all of the samples were coated with osmium. The average diameter of nanofibers was determined by analyzing the SEM images with an image analyzing software (Image-Pro Plus, Media Cybernetics Inc.). For the same samples of FE-SEM, the spectrum of energy dispersive X-ray spectroscopy (EDX) was applied to detect the introduction of SiO_2 on the membrane surface.

ATR–FTIR spectra of the samples were obtained with a Nicolet 5700 spectrophotometer (Thermo Electron Co.) in the wavenumber range 400–4000 cm^{-1}. X-ray diffraction (XRD) measurements were carried out to characterize the crystalline phase of PVDF–SiO_2 nanofiber membranes with a Panalytical X-ray diffractometer X'Pert Pro with Cu Kα radiation at 40 kV/30 mA. The diffractograms were scanned in a 2θ range of 10–70° at a rate of 2 ° min^{-1}. Furthermore, the crystallinity of nanofiber membranes was determined by a peak deconvolution method [17]. The diffraction peaks at 2θ = 18.5° and 20.7° were decomposed into amorphous and crystalline regions by a curve fitting technique. The crystallinity is defined as the area of crystalline phases divided by the total area of crystalline phases and amorphous phases as follows:

$$\text{Crystallinity}\,(\%) = \frac{A_c}{A_c + A_a} \times 100$$

where A_c is the area of the crystalline phase and A_a is the area of the amorphous phase.

The thermal properties of membranes were evaluated by differential scanning calorimetry (DSC, Q2000, TA Instruments) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere from 30 to 300 °C. From the DSC data, the crystallinity of the samples was calculated according to the following formula [18,19]:

$$\text{Crystallinity}\,(\%) = \frac{\Delta H_m^{sample}}{\Delta H_m^*} \times 100$$

where ΔH_m^* is the melting enthalpy for totally crystalline PVDF. Assuming the same melting enthalpy for all crystalline forms of PVDF, the melting enthalpy of 100% crystalline was given as 102.5 J g^{-1}.

Mechanical properties of membranes were assessed by a material testing system (Instron® 5565, Instron Co.) using a low force load cell of 10N capacity. Strip-shaped specimens (2 cm × 1 cm) were tested three times for each sample at a loading velocity of 10 mm min^{-1}. The membrane porosity was defined as the volume of the pores divided by the total volume of the porous membrane, which was determined by a mercury porosimeter (Pascal 440, Thermo Finnigan).

2.4. Electrochemical properties of nanofiber membranes

Electrolyte uptake by the membrane was assessed by soaking the membrane (2 cm × 2 cm) in the liquid electrolyte, 1 M $LiPF_6$ in EC/DMC (1:1, v/v). The weight of the wetted membrane was determined at different soaking intervals, taking care to remove the excess electrolyte remaining on the surface of the membrane by wiping softly with a tissue paper. The electrolyte uptake was calculated using the equation [13]:

$$\text{Electrolyte uptake}\,(\%) = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100$$

where M_{dry} is the mass of the dry membrane and M_{wet} is the mass after soaking in the liquid electrolyte.

An ionic conductivity cell was assembled by sandwiching a given polymer electrolyte between two stainless steel (SS) blocking electrode (2 cm × 2 cm), and was vacuum-sealed with a polyethylene-coated aluminum pouch. The ionic conductivities were measured by the AC impedance method of the SS/polymer electrolyte/SS at room temperature, using 1260A impedance analyzer (Solartron Analytical) over the frequency range of 100 mHz to 2 MHz.

3. Results and discussion

3.1. Electrospinning of PVDF–SiO_2 composite nanofiber membranes

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. In this study, 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.

Composite nanofiber membranes were prepared by electrospinning from PVDF–SiO_2 blend solutions with different SiO_2 contents. The contents of SiO_2 in the mixed solutions were 0 (PVDF), 3 (SIL-3), 5 (SIL-5) and 7 wt% (SIL-7) based on the weight of PVDF. The morphological structures of electrospun composite nanofiber membranes are shown in Fig. 1. The result nanofiber membranes exhibited a fully interconnected pore structure with narrow pore size distribution. The surface roughness increased with increasing the SiO_2 content, while the average diameter of nanofibers was rarely affected, which was ~490 nm. It was also observed that SiO_2 was uniformly distributed in the polymer matrix. EDX spectra confirmed the presence of SiO_2 on the external surface of the composite nanofiber membrane. The two peaks ascribed to silicon and oxygen atoms newly appeared by the addition of SiO_2 (Fig. 2).

ATR–FTIR analysis was carried out for surface characterization of the nanofiber membranes in the range of 400–1600 cm^{-1}. As shown in Fig. 3, three strong peaks centered at 1404, 880 and 1183 cm^{-1} were observed for PVDF membrane. The former two peaks were due to the C–F stretching vibration, and the latter one was due to the C–C bond of PVDF [20,21]. In addition, two weak bands appeared at 510 and 487 cm^{-1} were assigned to the CF_2 bending vibration. In