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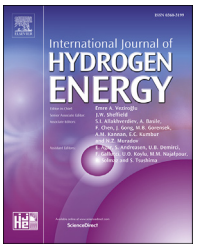

Permeability, thermal and wetting properties of aligned composite nanofiber membranes containing carbon nanotubes

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ABSTRACT

In this paper, aligned single wall carbon nanotubes/Polyacrylonitrile (SWNTs/PAN) nanofiber membranes were fabricated by a modified parallel electrode method (MPEM), in which a positively charged copper ring was placed between the needle and the parallel electrode collector. The permeability, thermal and wetting properties of aligned SWNTs/PAN membranes obtained by MPEM were investigated. And the experimental results showed that the addition of the SDBS-modified SWNTs could enhance hydrophilicity of PAN nanofiber membranes, and the alignment of composite membranes could improve the permeability and wetting properties. In addition, an illustration of wetting property was given through the geometric potential. The illustration was in good agreement with the experimental data, and showed the MPEM could make hydrophobic materials more hydrophobic and make hydrophilic materials more hydrophilic.

Introduction

Carbon nanotubes (CNTs) are famous as reinforcing material because of their amazing mechanical, conductive and thermal properties [1–5]. Therefore, a large group of scientists have been keen to develop the application fields of polymer/CNTs composites, such as bio-medical, electrochemistry, energy and the photoelectric fields [6–10].

Electrospinning (ES) is one of the most efficient methods for preparing CNTs/polymer composite nanofibers. The properties of the electrospun nanofibers are expected to be enhanced by stretching and making composites [11,12]. Many researchers have fabricated various CNTs/polymers composites [13–15]. However, randomly oriented composite nanofiber membranes (NFMs) with low mechanical and electrical properties are obtained by the traditional apparatus [16], which could limit their application. It is necessary to generate aligned composite NFMs to broaden the application fields, such as electrochemical sensors, reinforcements, optoelectronic devices, and so on.

In our previous work, we presented a modified parallel electrode method (MPEM) to fabricate highly aligned electrospun nanofibers, in which a positively charged copper ring was placed between the needle and the parallel electrode collector, see Fig. 1 [17,18]. In this article, permeability, thermal and wetting properties of aligned single wall carbon nanotubes/Polyacrylonitrile (SWNTs/PAN) NFMs obtained by

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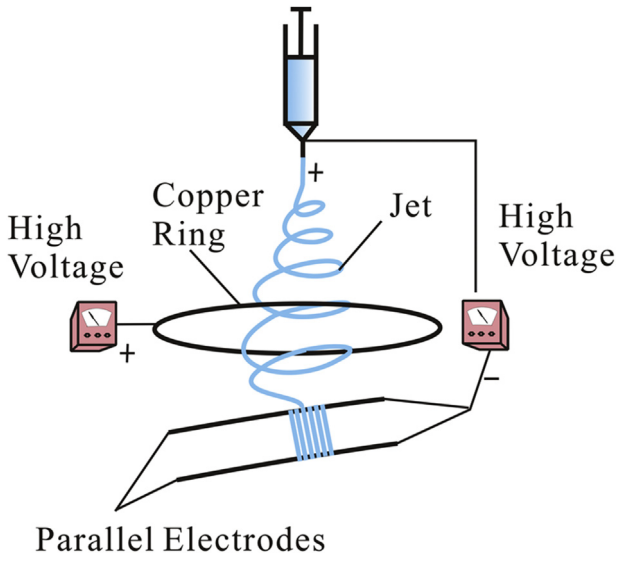

Fig. 1 – The apparatus of MPEM.

MPEM were investigated. The results showed that the addition of the SDBS-modified SWNTs could enhance hydrophilicity of PAN NFMs, and the alignment of composite NFMs obtained by MPEM could improve the permeability and wetting properties. Therefore, aligned SWNTs/PAN composite NFMs will be used as electrode or battery membrane in future.

Experimental

Materials

Polyacrylonitrile (PAN, M_W = 150,000) powder, was provided from Beijing Lark Branch Co., Ltd (Beijing, China). N, N-dimethylformamide (DMF), which could easily evaporate during the ES, was purchased from Shanghai Chemical Reagent Co., Ltd (Shanghai, China). Sodium dodecyl benzene sulfonates (SDBS), were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). And single wall carbon nanotubes (SWNTs) were supplied by Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China) (length: 5–30 μm, inner diameter: <2 nm, purity: ≥98%, ACOOH content: 2 wt%). All chemicals were of analytical grade and used without further purification.

Solution preparation

SWNTs of about 24 mg and SDBS of about 1 g were dispersed in 20 ml of DMF at room temperature (25 ± 2 °C) using an ultrasonic cleaner (SL-5200DT, Nanjing Shunliu Instrument Co., Ltd, Nanjing, China) for 4 h. That meant SWNTs were functionalized by SDBS treatment to improve dispersion in spinning solution. And the SDBS-modified SWNTs showed a good hydrophilic property. PAN of about 1.6 g was then dissolved in SWNT-dispersed DMF solution with the 1.5 wt% SWNT concentration under magnetic stirring for 6 h at room temperature until it became homogeneous. For comparison, PAN solutions were prepared with 8 wt% by using DMF. These polymer solutions were used for ES and MPEM.

Fabrication of electrospun PAN and SWNTs/PAN NFMs

MPEM and ES experiments were carried out at room temperature (25 ± 2 °C) at a relative humidity of 50%. The prepared spinning solution was dropped into a 10 mL syringe. The flow rate was 0.5 mL/h. The applied spinning voltage was 15 kV, and the applied ring voltage was +5 kV. The distance from the tip of the needle to the parallel auxiliary electrodes was 18 cm, and the distance from the ring to the parallel electrode collector was 5 cm. The diameter of the copper ring was 21 cm, and the gap between two parallel auxiliary electrodes was 4 cm. Highly aligned PAN and SWNTs/PAN NFMs were fabricated directly by MPEM, and randomly oriented PAN and SWNTs/PAN NFMs were prepared by ES.

Measurements and characterizations

Scanning electron microscopy (SEM)
The morphologies of SWNTs/PAN composite NFMs obtained respectively by ES and MPEM were observed by a scanning electron microscopy (SEM, Hitachi S-4800, Tokyo, Japan) at an acceleration voltage of 3 kV. And the nanofibrous diameter distributions were analyzed with ImageJ software (National Institute of Mental Health, Bethesda, Maryland, USA).

Thermogravimetric analysis (TGA)
In order to characterize the thermal decomposition profiles of both PAN and SWNTs/PAN NFMs obtained respectively by ES and MPEM, TGA was performed on a Diamond TG/DTA5700 (PerkinElmer, USA). Dry specimens of either PAN or SWNTs/PAN composites were measured with a nitrogen flow rate of 50 ml/min and at a heating rate of 10 °C/min in a temperature range from room temperature to 800 °C. The measurement was repeated three times.

Gas permeation test
The pore size distributions of PAN and PAN/SWNTs NFMs were measured using a capillary flow porometry (Porometer 3G, Quan-tachrome Instruments, USA). All samples were circular membranes with the diameter of 25 mm and the thickness of 10 μm. The Porofil had been selected as the wetting liquid because of its special physical properties. The Porometery 3G can expel the wetting liquid from through-pores in the sample. Gas pressure was automatically applied to one side of the sample. As pores emptied the resulting gas flowed through the open pores, gas pressure was accurately measured by the on-board microprocessor. And the results would be shown on the screen of the computer. The actual pressure at the sample was measured independently of the pressure control circuit to ensure the highest quality data.

Contact angle (CA) measurements
The wetting properties and static CAs of both PAN and SWNTs/PAN NFMs obtained respectively by ES and MPEM were investigated using a Krüss DSA 100 apparatus (Krüss Company, Germany). The volume of droplet used for static CA

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