Preparation of the nafion/CNT nanofibers via electrospinning

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Abstract. In this paper, we report the preparation of the Nafion/CNT nanofibers via electrospinning. PEO was added as carrier polymer to enhance the chain entanglements and therefore the electrospinnabilities of the nafion solution. Effects of the molecular weights of PEO on the electrospinnability were investigated. Three CNT samples, the CNT, CNT-150 and CNT-500 obtained from the ball-milling of the CNTs, were used and their particle size distributions were analyzed. Dispersions of the CNT, CNT-150 and CNT-500 in water and absolute ethanol were evaluated. Hexadecyl trimethyl ammonium bromide (CTAB) was used to disperse the CNT to single particle. The CNT-500, with the lower average particle size of 298.2 nm and the PDI of 0.167, shows the best dispersion in water and ethanol solution. The nafion/CNT-500 nanofibers were prepared via electrospinning by adding PEO and have better electrospinnability and morphologies.

1. Introduction
Nafion, a perfluorinated sulfonic acid polymer, is an important polymer electrolyte membrane in fuel cells, water electrolysis, chlor-alkali electrolyzers and superacid due to its excellent thermal, mechanical and chemical stability and high proton conductivities (~0.1S/cm) [1]. Commercially, nafion is available in several forms, such as extruded and solution cast films, dispersions in water/alcohol solutions and pellets. Several researches [2, 3] reported that the nafion fuel cell performance can be improved by scaling down nafion on the size scale of nanometers, especially nanofibers, due to the increasing ultrahigh specific surface areas.

Recently, nafion has been explored in sensor and actuators [4]. The IPMCs, one of the promising electroactive polymers, can generate fast and large bending deformation under the low electric fields [5] and be applied as biomimetic actuators for underwater propulsion [6] and micro-robots [7] and sensors for fluid flow [8], touch [9] and force [10]. IPMC is typically composed of a polyelectrolyte sandwiched with two metal electrodes. Nafion is one of the most-widely used polyelectrolytes in IPMCs. The shortcomings of the nafion-based IPMCs are low driving force and short life in air [11]. The actuating performances of IPMCs are influenced by the types of polyelectrolytes, electrodes and the interface between the polyelectrolytes and electrodes [12].

Carbonaceous materials possess good electric conductivity and mechanical properties. Black carbon, carbon nanotubes (CNTs), graphene, fullerenes and carbon nano-fibers are the common carbonaceous materials [13-14]. Palmre reported the nafion-based IPMCs with the highly porous carbon layers using DAP method show the better actuation performances due to the higher specific areas and the consequent larger charge-storage abilities [15]. Cho and Lee reported that more than seven layers stacked CNT-nafion IPMCs enhanced the maximum force with the increasing CNT concentration [16]. Significantly, the dispersion of the CNTs in nafion matrix is a key to enhance the
performance of the nafion-based IPMCs because the CNT aggregates diminish the adherence to the nafion matrix and concentrate stresses. Lian prepared the oxidized CNT by esterification with PEG to obtain the homogenous CNT-nafion membranes and actuators, which manifests more than 2 times increase in maximum blocking force [17].

Electrospinning is a popular technique to produce polymer nanofibers [18]. Few literatures reported the electrospinning of the nafion nanofibers because of the low viscosity and negligible chain entanglement regardless of polymer concentration, solvent type, neutralization, or electrospinning conditions [19]. Sanders prepared the electrospayed nafion films [20], which are similar to the extruded and cast nafion films in water uptake, dimensional changes and electrical conductivity.

To successfully electrospin the nafion solution, at least 12 wt% of the carrier polymer, such as poly (ethylene oxide) (PEO) [21], poly (vinyl alcohol) (PVA) [22], poly (acrylic acid) (PAA) [23] and polyaniline [24] have been required. Bin Dong reported the successful fabrication of high-purity nafion nanofibers (~99.9 wt%) via electrospinning with PEO (M_w=8000 kg/mol), which shows a higher proton conductivity of 1.5 S/cm than the bulk nafion film (~0.1 S/cm).

In this paper, we report the fabrication of the nafion/CNT nanofibers via electrospinning. PEO was added as carrier polymer to enhance the electrospinnability of the nafion solution. Two kinds of PEO, with the molecular weight of 4000 kg/mol and 500 kg/mol were used to investigate the effect on the electrospinning of the nafion solution. The CNTs were added to improve the conductivity of the nafion nanofibers. The obtained experimental results are significant in manufacture and enhancement of the actuating performances of the IPMCs.

2. Experimental

2.1. Materials
5wt% nafion solution was purchased from Dupont Company, and MWCNTs were purchased from Tanfeng Technology, Suzhou, China. PEO with the molecular weight of respectively 4,000,000 and 500,000 were purchased from Kaiyuan Chemical and Technical Co. Ltd. Hexadecyl trimethyl ammonium bromide (CTAB) was purchased from Damao Chemical Reagent Company, Tianjin, China. All the reagents were used as received.

2.2. Ball-milling of the MWCNTs
MWCNTs were ball milled into the nano-scale by Pulverisette7 high energy ball mill. MWCNTs and quartz balls with the mass ratio of 1:20 were divided equally into two parts and respectively placed into two milling jar. Before milling, the milling jar was vacuumized and then inflated with 0.3 MPa argon gas for 20 s. The ball milling rotating velocity was set as 150 rpm or 500 rpm to obtain the CNT-150 or CNT-500. Milling was performed for 30 min and repeated 12 times. For each milling, the milling jar was rotated for 20 min and then stopped for 10 min to avoid overheat generated by the friction.

2.3. Preparation of the nafion nanofibers by electrospinning
Certain amounts of 5 wt% nafion, CTAB and CNT-500 were mixed, ultrasonic vibrated for 45 min and then PEO was added. The obtained solution was stirred at room temperature for 5 h. The mixture was electrospun at room temperature. Positive voltages applied to the polymer solutions were in the range of 10~16 KV. The inner diameter of the electrospinning needle was 0.5 mm. The electrospinning distance between the tip of the needle and the collector was 15 cm and the rotating rate of the collector was 120 rpm. The nafion solution flow rates were controlled by a syringe pump ranging from 0.2~0.5 mL/h.

2.4. Particle size analysis of the CNTs
0.015 g CNTs and 0.05 g CTAB were added into 20 mL deionized water or absolute ethanol. The obtained mixture was ultrasonic vibrated for 45 min by KQ2200DB ultrasonic cleaner with the heating
temperature of 40 °C and vibration power of 99 %. The ultrasonic vibrated CNTs solutions were examined by Malvine Nano-ZS90 Particle Size Mete to provide the particle size data.

2.5. TEM
0.0011 g CNTs were ultrasonic vibrated in 20 mL absolute ethanol solution for 45 min at room temperature with the vibration power of 99 %. The vibrated CNT solution was examined by the Hitachi H7650 transmission electron microscopy to observe the morphologies of the CNTs.

2.6. SEM
Morphologies of the obtained nafion nanofibers were measured by the Hitachi S4800 field emission scanning electron microscopy. Before the FESEM observation, the nanofibers were gold-sprayed.

3. Results and discussion

3.1. Ball-milling of CNTs
The MWCNTs were ball-milled respectively by 150 rpm and 500 rpm to obtain the samples, expressed as CNT-150 and CNT-500. The MWCNTs without being ball-milled were used as a reference. Figure 1(a) shows that the CNTs possess the typical hollow structure with the length of 1.4 μm and the diameter of 20 nm. Figure 1(b) reveals that the CNT-150, which was prepared after being milled for 6 h, has been broken into a nano-scale with the length range of 300~700 nm. These indicate the ball-milling can effectively decrease the length of the CNTs and never destroy the hollow structure.

![Figure 1. TEM images of CNTs (a) and CNT-150 (b).](image)

3.2 Dispersion of the CNTs
When the CNTs were added into the nafion solutions, the nano-particle aggregation has to be considered. A common way is to use surfactants to diminish the surface energy of the CNTs to reduce the aggregation. In this paper, CTAB was used as a surfactant. Because the 5wt% nafion solution is mainly composed of water and 1-propanol, water and ethanol were respectively used as the medium to disperse the CNTs.

![Figure 2. Dispersion of the CNT, CNT-150 and CNT-500 in water(a) and absolute ethanol(b).](image)

Figure 2 manifests the CNT dispersion in water and ethanol. Three samples of CNT, CNT-150 and CNT-500 were respectively ultrasonic vibrated to obtain a bright black solution in either water or
absolute ethanol. In the case of water as the dispersion medium, after two weeks, many CNT depositions were found on the bottom of the glass bottle. However, the solutions of CNT-150 and CNT-500 still retained black. When the absolute ethanol was used as a dispersion medium, after 3 h, CNT and CNT-150 were observed to aggregate and precipitate. The solution of CNT-500 still shows the black colour.

The CNT dispersion experiments indicate that the dispersion of CNTs in water is better than in ethanol. The CNT-500 shows the best dispersion, then the CNT-150, and the CNT manifests the worst.

3.3 Particle size distribution of the CNTs

In this section, the effect of ball-milling on the diameter of the CNTs was evaluated. Figure 3 shows the particle size distribution of the CNT, CNT-150 and CNT-500 in water. The particle size distribution curve of the CNTs has two peaks, respectively at 150 nm and 1500 nm, with the average particle size of 492.2 nm and polymer dispersity index (PDI) of 0.611. The CNT-150 has three peaks respectively at 10 nm, 350 nm and 1700 nm, with the peak area being increased in proper order. The CNT-150 has the average diameter of 386.6 nm and PDI of 0.483. The CNT-500 shows a single peak at 400 nm with the particle size of 298.2 nm and PDI of 0.167.

These results manifest that the ball-milling can effectively influence the particle size of the CNTs. The greater the rotation rate of the ball-milling is, the smaller the particle size of the CNT is.

3.4 Electrospinning of the nafion and CNTs

Because the 5wt% nafion solution has a lower viscosity and never be electrospun alone, the polymers such as PEO, PVA and PAA have to be added to enlarge the chain entanglement to obtain an appropriate spinning solution. In this paper, two kinds of PEO with the molecular weight of 4,000,000 and 500,000 were respectively added into the nafion solution to adjust the viscosity. On the other hand, due to the lower particle size and better dispersion in water, CNT-500 was chosen to improve the conductivity of the nafion fibers in place of CNT and CNT-150.

Figure 4 manifests the SEM images of the nafion/CNTs nanofibers by electrospinning. Figure 4(a) shows when the PEO with the molecular weight of 4,000,000 is used, the nafion solution presents a great viscosity and is hardly extruded from the spinning needle. Therefore, few nanofibers were collected and scattered on the receiving drum. When the PEO with the molecular weight of 4,000,000 and CNT-500 were used together in figure 4(b), the obtained nanofibers became thick in diameter, even adhered together, indicating a too great viscosity of the polymer solution, which furthermore causes an incomplete solidation of the nafion nanofibers during the electrospinning process.

Adding the PEO with the molecular weight of 500,000 makes the electrospinning of the nafion solution smoother and the obtained nanofibers possess the better fibrous structure in figure 4(c). Furthermore, when CTAB, as a surfactant to improve the dispersion of CNT-500 in the nafion solution, and CNT-500 were added, the electrosprinning could be performed. Fewer broken ends and beaded morphologies on the nanofibers are observed in figure 4(d).
4. Conclusions

Composite nafion/CNT nanofiber mats were fabricated via electrospinning with potential application as polyelectrolytes in IPMCs. Effects of CNT particle size on the dispersion were evaluated. The CNT-500, prepared from ball milling of CNTs with the lowest particle size reveals the best dispersion in water and ethanol. PEO was added as the carrier polymer to improve the electrospinnability of the nafion solution. Compared with PEO with the molecular weight of 4,000,000, PEO with the molecular weight of 500,000 manifests the better electrospinnability and the resulted nafion/CNT fibers show better fibrous shape.

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