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Ionic polymer–metal composite actuator based on sulfonated poly(ether ether ketone) with different degrees of sulfonation

Yongjun Tang, Zhigang Xue*, Xiaolin Xie, Xingping Zhou*

Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

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ABSTRACT

The sulfonated poly(ether ether ketone) (SPEEK) membranes with different degrees of sulfonation (DS) were prepared for fabricating high-performance ionic polymer–metal composite (IPMC) actuators. The ion exchange capacity (IEC), water uptake and ion conductivity of SPEEK membranes increase accordingly with the increase of the DS of SPEEK membranes. The SPEEK membranes show much higher IEC and water uptake than those of the traditional Nafion membrane. The SPEEK actuator with the highest DS, namely SPEEK3 actuator, shows the best bending deformation under the electric stimulus. Compared with Nafion system, the SPEEK3 actuator increases at maximum blending strain under sinusoidal voltage of 3 V at 1 Hz. These greatly enhanced actuation performance indicates the SPEEK is a candidate to substitute Nafion in the field of IPMC actuator.

1. Introduction

Ionic polymer–metal composite (IPMC) has attracted much attention owing to its unique actuation and sensing capabilities [1–4]. IPMC is attractive for potential applications in soft actuators, soft sensors and artificial muscles [5–7], owing to its flexibility, light weight, easy miniaturization, and rapid response. IPMC actuator can exhibit a large bending strain under a low applied voltage.

The IPMC has a sandwich-like configuration, typically consisting of an ion exchange membrane covered by two layers of thin metal electrodes on both surfaces through the impregnation-reduction method. When a hydrated cantilever strip of IPMC is subjected to a low driving voltage, the IPMC undergoes a fast bending deformation toward the anode. Conversely, charge in term of voltage or current will be produced between two sides of IPMC if the IPMC is stimulated by mechanical bending deformation.

In the IPMC actuator, the composition, nature and morphology of ion exchange membrane is able to affect the performance of the resulting IPMC actuator. The most widely used polyelectrolyte membrane [8–10] in IPMC actuator is Nafion, because it has excellent chemical stability and high proton conductivity. The Nafion-based IPMC actuator can show good actuation performances under electric voltage stimulus. However, the high cost, environment-unfriendliness, low water-retention capability, low actuation force, and back-relaxation under direct current (DC) voltage limit Nafion's practical applications. Therefore, many easily synthesizable and inexpensive polyelectrolyte membranes have been used in IPMC actuators to replace Nafion membranes [5–7].

Like Nafion, fluorinated polymers [11,12] were not cheap and not environmentally-friendly. The industrial-grade polymers, such as nonfluorinated hydrocarbon polymers and a few fluorinated polymers, have been used to develop novel IPMC actuators after simple chemical modification. In these polymers used in IPMC actuators, lots of sulfonated polymers [13–37] were easily synthesized, so they can be used as cost-effective and high-performance ionic membranes for IPMC actuators.

Sulfonated poly(ether ether ketone) (SPEEK) has been successfully used as proton exchange membrane in the field of fuel cell [38,39] owing to its excellent mechanical and chemical stability, good film-forming capacity, high ionic conductivity and low price. Jeon et al. [26] synthesized an electro-active polymer membrane based on the SPEEK/poly(vinylidene fluoride) (PVDF). The actuation performance can be adjusted by controlling the swelling ratio by the compositions of SPEEK and PVDF. However, the high degree of sulfonation (DS = 95%) of SPEEK used in their work resulted in high water uptake and fragile membrane in dry state. The incompatibility of hydrophilic SPEEK and hydrophobic PVDF affected the

* Corresponding authors. Fax: +86 27 87543632.
E-mail addresses: zgxue@mail.hust.edu.cn (Z. Xue), xpzhou@mail.hust.edu.cn (X. Zhou).

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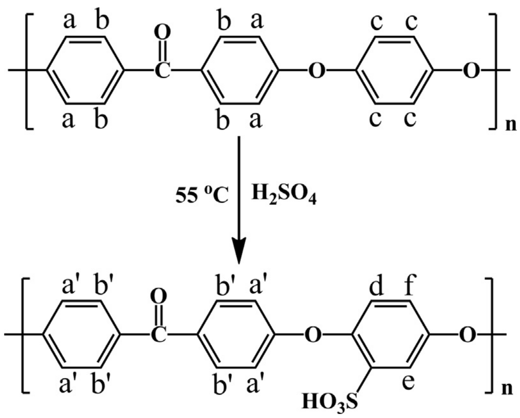

Fig. 1. Reaction scheme of sulfonation of PEEK.

properties of SPEEK/PVDF blend membrane. Furthermore, only very few studies concentrated on the effect of DS or IEC of polyelectrolyte membranes on the electromechanical response for the IPMC actuators [13–37]. In this study, SPEEK was synthesized through post-sulfonation, and used to prepare IPMC actuator by solution-casting and subsequent chemical plating of metal electrodes. Three kinds of SPEEK membranes with different DS were synthesized, and their ion exchange capacity, water uptake, ionic conductivity, mechanical properties were also studied. The electromechanical performances of the as-prepared IPMC actuators in term of bending displacement under DC and AC voltages were investigated according to their DS and compared with the Nafion counterpart.

2. Experimental

2.1. Materials

Poly(ether ether ketone) (PEEK, Victrex 450 PF, M_w = 38,300) was purchased from Victrex Company (UK), and vacuum dried at 100 °C overnight prior to use. Tetraamineplatinum chloride hydrate ($[Pt(NH_3)_4]Cl_2$) was provided by Aladdin Industrial Inc., China. All other chemicals were supplied from Sinopharm Chemical Reagent Co., Ltd., (China) and used as received without further purification.

2.2. Preparations of SPEEK and SPEEK membranes

Typically, the dried PEEK (15 g) was completely added in 450 mL of H_2SO_4 at 55 °C under vigorous stirring. The SPEEK was obtained by pouring all the reaction solution into a large amount of ice. The product was filtered and washed with DI water repeatedly until a neutral pH level.

The SPEEK membranes were prepared by the solution casting method. Firstly, the SPEEK was dissolved in *N*,*N*-dimethylacetamide (DMAc) to make a 25 wt% homogeneous solution. The solution was then cast onto a clean glass plate and spread thoroughly by using a doctor blade with 600–700 μm gap. The solvent was removed by first air drying at 35 °C for 12 h, then drying at 65 °C and 85 °C for 2 h respectively, and finally followed by further drying at 135 °C for 3 h. Moreover, in order to reduce water uptake and keep dimensional stability of the SPEEK membrane with the highest degree of sulfonation (namely SPEEK3 membrane), SPEEK3 membranes were subjected to further heat treatment (i.e. drying at 155 °C for 3 h). The resulting membranes were peeled off from the glass plate. The thickness of dried SPEEK membranes was measured in the range of 110–120 μm with a digital micrometer. Following the increasing order of sulfonation time, SPEEK membranes were named sequentially as SPEEK1 (2 h), SPEEK2 (2.5 h), and SPEEK3 (3.5 h), respectively.

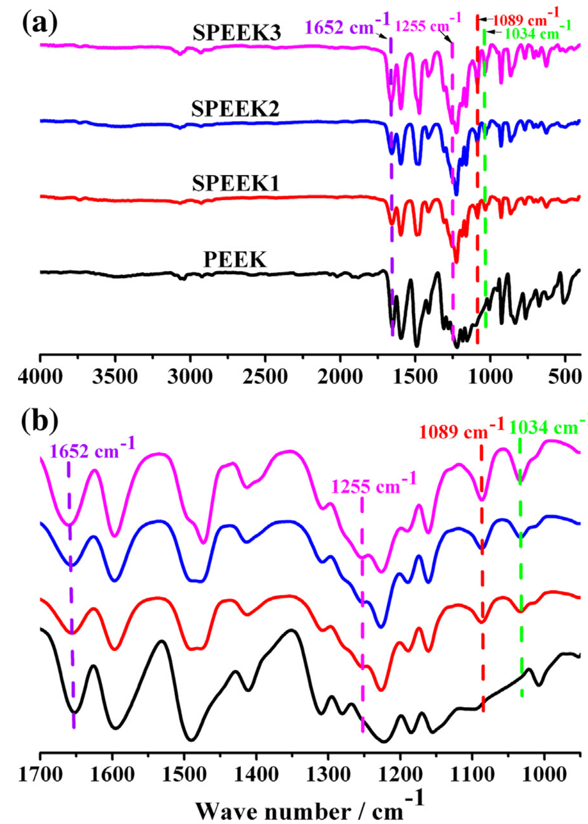

Fig. 2. FTIR spectra of PEEK and SPEEK: the full spectra (a), and magnified local detail (b).

2.3. Preparation of IPMC actuators

SPEEK-based IPMC actuators were fabricated by an electroless plating method as described in Refs. [36,37].

2.4. Characterization

FTIR spectra were recorded on an Equinox 55 spectrometer (Bruker) in the range of 4000–400 cm^{-1}. The samples were prepared by casting several drops of polymer solutions (2 wt%) onto KBr pellets and dried in oven. ^{1}H NMR spectra were performed by a Bruker AV400 NMR spectrometer with deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent and tetramethylsilane (TMS) as the standard.

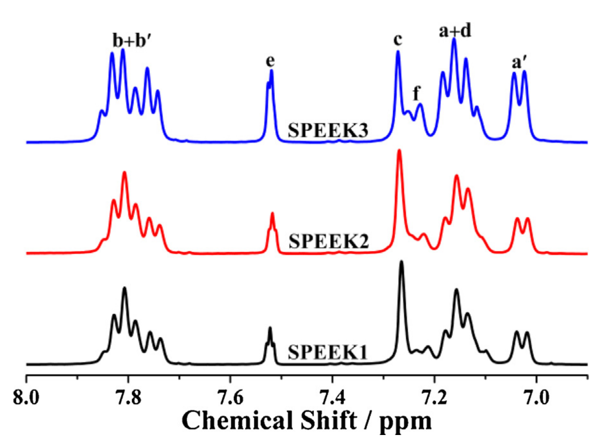

Fig. 3. ^{1}H NMR spectra of SPEEK.