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Electro-Active Polymer Actuator by Employing Ionic Networking Membrane of Poly (styrene-*alt*-maleic anhydride)-Incorporated Poly (vinylidene fluoride)

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ABSTRACT

In this study, a novel actuator was developed by employing the newly-synthesized ionic networking membrane (INM) of poly (styrene-*alt*-maleic anhydride) (PSMAn)-incorporated poly (vinylidene fluoride) (PVDF). Based on the same original membrane, various samples of INM actuator were prepared through different reduction times with the electroless-plating technique. The as-prepared INM actuators were tested in terms of surface resistance, platinum morphology, resonance frequency, tip displacement, current and blocked force, and their performance was compared to that of the widely-used traditional Nafion actuator. Scanning electron microscope (SEM) and transmission electron microscopy (TEM) revealed that much smaller and more uniform platinum particles were formed on the surfaces of the INM actuators as well as within their polymer matrix. Although excellent harmonic response was observed for the newly-developed INM actuators, this was found to be sensitive to the applied reduction times during the fabrication. The mechanical displacement of the INM actuator fabricated after optimum reduction times was much larger than that of its Nafion counterpart of comparable thickness under the stimulus of constant and alternating current voltage.

1. Introduction

In recent years, significant research efforts have been focused on the development of new smart materials, which responds to external stimuli and can be utilized in biomimetic motions [1]. Of all the candidates that may materialize the action of natural muscles, electroactive polymers (EAPs) attract considerable attention from the materials research community.

Among EAPs, IPMC is considered to be the most promising one for artificial muscle due to its large bending displacement in the presence of a low applied voltage. However, the review of the current open literature reveals that functional IPMC applications have been focused almost exclusively on the class of perfluorosulfonated ionomers, such as Nafion® from Dupont. Even though the actuators by employing the perfluorinated ionic polymers as ion-exchange membranes have demonstrated good performance during the electromechanical test, there are still certain disadvantages that hinder them from wide applications. So many efforts has been undertaken to replace the most widely used Nafion family in polymer actuators by cheaper and ecologically more acceptable materials over the past few years. So far, the work done has been only partially successful. Employing the membranes prepared through the conventional methods by these academic and industrial groups, the electromechanical performance of the actuators was not comparable with that of their Nafion counterpart. Therefore, to develop artificial muscles with improved performance and unique characteristics, an actuator based on the membrane resulting from a new methodology is particularly required.

Herein, we report on the development of a novel actuator by employing the ionic networking membrane (INM) of poly (styrene-*alt*-maleic anhydride) (PSMAn)-incorporated poly (vinylidene fluoride) (PVDF). Based on the same original membrane, various samples of INM actuator were prepared through different reduction times with the electroless-plating technique. The as-prepared INM actuators were then tested in terms of surface resistance, platinum morphology, resonance frequency, tip displacement, current and blocked force, and their performance was compared to that of the widely-used traditional Nafion actuator.

2. Experiments

2.1 Preparation of Ionic Networking Membranes

The ionic networking membrane (INM), composed of styrene-maleimide alternating

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polymer (PSMAn) and vinylidene fluoride polymer (PVDF), has been prepared by using 2,2' -benzidinedisulfonic acid-triethylamine (BDSA-TEA) salt.. The synthesis of INM was performed by two-pot systems as follows. First, the mixture of polyamic acid (PAA)/DMSO, composed of two polymers (PSMAn/PVDF) and BDSA-TEA salt, was carefully cast on a glass plate, and then the plates were placed in a vacuum oven at 60°C for 48 h to slowly remove most of the solvent. The film was thermally imidized with increasing temperature at 150 °C for 12 h, 180 °C for 6 h, and finally 240°C for 1 h under vacuum to remove residual solvent. The resulting membrane was detached from the glass plate, and then immersed into 1M sulfuric acid (H_2SO_4) overnight so that the salt form of BDSA was converted into acid form, followed by washing with deionized water several times until it reached neutral pH. Finally, the membrane is composed of crosslinked imide segments with sulfuric acid groups.

2.2 Fabrication and Characterization of Actuators

Platinum (Pt) electrodes were created on both surfaces of the membranes through the electroless plating process described in the literature [2]. SEM observations were carried out with a HITACHI S-4700 instrument attached with an energy dispersive X-ray microanalysis (EDX). TEM detections were performed with a JEM-2000 FX-II apparatus by employing a MT7000 CR microtome for the preparation of ultrathin sections through room-temperature microtomy. For the electromechanical test, the reduced membranes were cut into strips with dimensions of 5mm in width and 30mm in length except these denoted specially. The experimental setup was composed of a laser displacement measurement system (Keyence, LK-031), and a National Instruments PXI system. All the data acquisition and control are accomplished with an industrial computer by using LabView® program. To determine the resonance frequency, the frequency responsive function (FRF) test was performed by the swept-sine method under water, and the applied exciting voltage was 0.05V.

3. Results and Discussion

Fig. 1 shows the strips of PSMAn-incorporated PVDF before and after Pt electroless-plating. Compared with its Nafion counterpart, although the prepared membrane of PSMAn-incorporated PVDF is endowed with slightly smaller water uptake together with lower proton conductivity, its ionic-exchange capacity (IEC) is much higher. The surface resistance of the INM actuators decreased with the increment of the reduction times, which may indicate the more improved efficiency of the beam motion. It can also be observed that the ohmic value of INM 3, which was fabricated through only 3 primary reductions, was smaller than the referenced Nafion actuator prepared after 3 primary reductions and 1 secondary reduction. This should possibly be assigned to the high intrinsic IEC of the membrane of PSMAn-incorporated PVDF. The resonance frequency of the INM beams was increased from 1.61 to 2.11 Hz and 2.61 Hz as the plating times increased from 1 to 2 primary reductions and 3 primary reductions and 1 secondary reduction. This accords with the common principle, because the resonance frequency generally increases with the beam thickness on condition that the actuators are made from the same original membrane material.

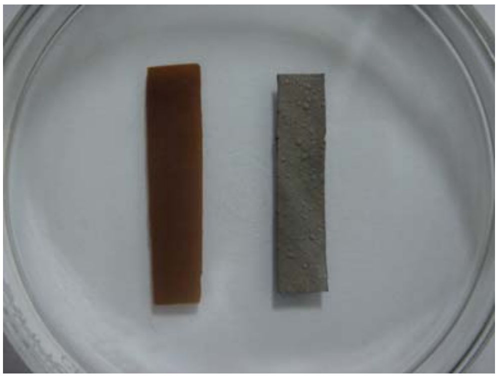

Fig. 1 The strips of the PSMAn-incorporated PVDF before (left) and after (right) Pt electroless-plating. 3 primary reductions and 1 secondary reduction were applied during the fabrication of the INM actuator.

The time-displacement curves of the as-prepared actuators of INM 1, INM 2 and INM 4 under the excitation of 0.5V DC voltages are given out and compared to that of the Nafion-based one (NM) in Fig. 2. The displacement of the INM beams increased along with the increment of the applied time, which showed the same tendency as that of the Nafion strip during the first several seconds. However, the Nafion beam straightened back almost immediately after a relative faster response, while the INM strips retained the force up to 225 s, and exhibited several times larger displacement than its Nafion counterpart under the same magnitude DC stimulus. The slow relaxation of the strain for Nafion actuator was commonly thought to be due to the diffusing back of water to the anode side as a result of relatively small amount of water movement. The applied reduction cycles were found to strongly affect the performance of mechanical displacement as well. The actuator of INM 2 was obtained after 2 primary reductions, but the observed tip displacement was much larger than that of INM 1 prepared through 1 primary reduction, which should be assigned to the reduced surface resistance resulting from a deeper penetration depth. The INM 4 was endowed with the best surface conductivity after 3 primary reductions and 1 secondary reduction, and was expected to display the largest displacement among the fabricated INM actuators. Nevertheless, the result only revealed a slightly higher value in this actuator if compared with that of INM 1. The unexpected results may possibly be ascribed to the thickness of the created electrodes. The thickness of the Pt layers for each actuator increased along with the increment of the reduction cycles, which resulted in higher and higher bending stiffness. When the thickness was too thick, the displacement was rather decreased, since the bending stiffness for an actuator such as INM 4 was so high that it is difficult to be bent by the electrical activation. Therefore, the results indicated that the intrinsic properties of the original membrane and the reduction process should be considered comprehensively during the fabrication of the INM actuators so as to attain the satisfactory actuation performance.

The blocked force of the fabricated actuators was tested under 2.0V DC stimulus, and the results were listed in Table 2. The forces of the INM actuators constructed with the films prepared in the current study increased along with the increment of the reduction times. This is mainly due to the thicker deposited platinum layers, which increased the mechanical stiffness of the INM strips. As discussed above, the excessively increased stiffness also decreased the displacement. Although the generated force is determined comprehensively by the stiffness and the displacement, there should be a factor that plays the prominent role under certain conditions. In this experiment, the mechanical stiffness may be the central issue in controlling the output blocked force.

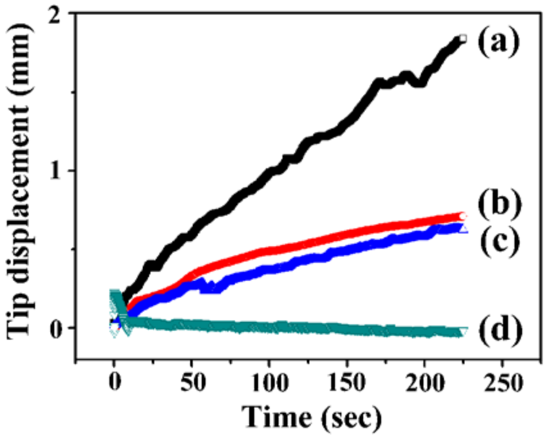

Fig. 2 Displacement of the actuators of the PSMAn-incorporated PVDF and Nafion 117 recorded for 225s with an applied DC excitation of 0.5V: (a) INM 2; (b) INM 4; (c) INM 1; (d) NM. The displacement was measured at a point 20mm away from the grip.

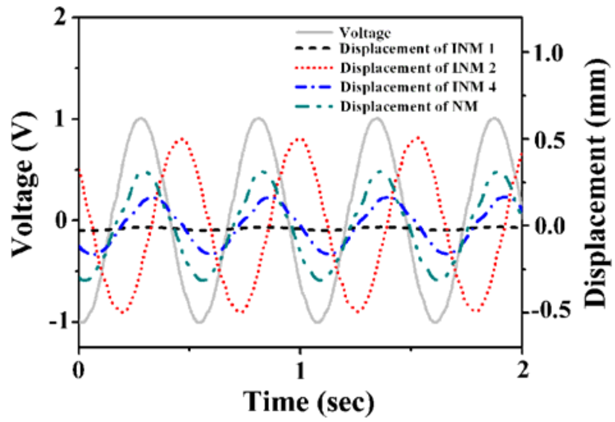

Fig.3 Displacement of the actuators of INM 1, INM 2, INM 4 and NM at 2.0Hz sinusoidal wave signal with 1.0V amplitude. The displacement was measured at a point 20mm away from the grip.

Fig. 3 gives out the harmonic responses of tip displacement of the actuators of INM 1, INM 2, INM 4 and the referenced NM at 2.0Hz sinusoidal wave signal with amplitude of 1.0 V. The beam INM 1 simply showed negligible motion under the excitation of the applied relative lower voltage of high frequency. However, reduced once again, the fabricated strip of INM 2 displayed much larger displacement, the value of which even considerably exceeded that of the widely-used Nafion actuator. Just as the case in the DC test, the measured displacement value of INM 3 prepared through 3 primary reductions and 1 secondary reduction was found to be between that of INM 1 and INM 2. This should also be ascribed to the increased bending stiffness caused by the increment of the reduction cycles. Another phenomenon noted is that the tip displacement of the INM beams lagged if compared with the applied voltage, which was mainly due to the capacitance characteristic of the fabricated actuators. Nevertheless, to increase the reduction cycles can result in more synchronous response of displacement for the INM strips. As can be seen, the mechanical displacement of INM 4 showed lower phase shift that of INM 2 from the same applied voltage signals.

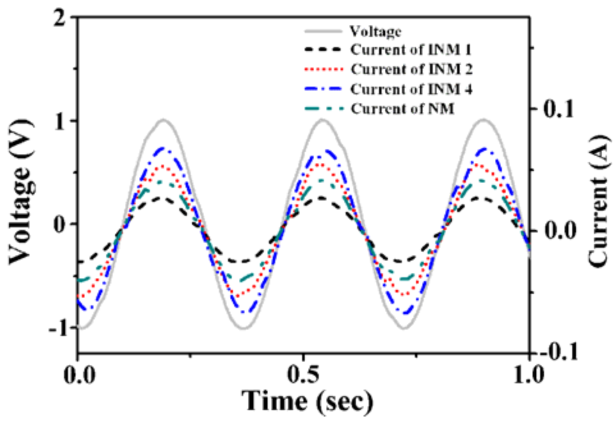

Fig . 4 Harmonic responses of the electrical currents at 3.0Hz sinusoidal input signal with 1.0V amplitude for INM 1, INM 2, INM 4 and NM.

The current responses of the actuators of INM 1, INM 2, INM 4 and the referenced NM were recorded at 3.0Hz sinusoidal input signal with 1.0V amplitude, and the results are shown in Fig. 4. The measured electrical currents of the as-prepared INM actuators were almost synchronous with the applied signal of high frequency. The current value increased with the increment of the reduction cycles, which is consistent with the determined ohmic data of surface conductivity. Although the surface resistance of INM 2 is somewhat larger than that of the referenced NM, its current response was still stronger. This phenomenon may possibly be ascribed to the different inherent nature of the employed original membranes: one was from the ionic networking membrane of PSMAn-incorporated PVDF, and the other was from the traditional film of Nafion 117.

4. Conclusions

In summary, a novel actuator was developed by employing the newly-synthesized ionic networking membrane of PSMAn-incorporated PVDF. SEM and TEM revealed good micromechanical morphology of the as-prepared actuators fabricated through the electroless-plating technique. The applied reduction cycles were found to strongly affect the properties of INM beams in terms of surface resistance, platinum morphology, resonance frequency, tip displacement, current and blocked force. In addition to the nice harmonic response, the mechanical displacement of the INM actuator fabricated after optimum reduction times was much larger than that of its Nafion counterpart of comparable thickness under the stimulus of constant and alternating current voltage.

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