Available online at www.sciencedirect.com

SCIENCE DIRECT®

Synthetic Metals 153 (2005) 121–124

SYNTHETIC METALS

www.elsevier.com/locate/synmet

Fabrication and evaluation of actuators based on polymer electrolyte membranes

T. Nakano, Y. Takeoka, M. Rikukawa*, K. Sanui

Department of Chemistry, Sophia University, 7-1, Chiyoda-ku, Tokyo 102-8554, Japan

---

Abstract

Actuators based on hydrocarbon polymer electrolyte membranes having phosphoric acid groups were fabricated to investigate the correlation between the chemical properties and the actuation. The bending size and velocity of actuation were measured and compared with the values for fluorocarbon polymers, Nafion®-based actuators. The actuators were fabricated by coating polymer electrolyte membranes with gold using dichlorophenanthrolinegold (III) chloride. The actuators bent toward the anode when the applied voltage was over 1 kV. Nafion®-based actuators reached the maximum displacement size within 1 second, while the hydrocarbon polymer-based actuators took over 60 seconds. The difference in the velocity of actuation was caused by the difference in the proton conductivity of polymer electrolyte membranes. The maximum displacement size of hydrocarbon polymer-based actuators was nearly equal to that of Nafion®-based actuators.

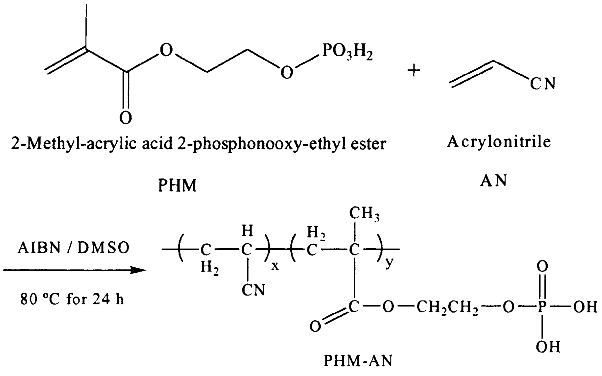
Keywords: Conducting polymer, Amorphous thin films, Metal/electrolyte interfaces, Switches

---

1. Introduction

Recently, novel actuators based on polymer materials have attracted a lot of interest as the artificial muscle. These devices are expected to apply to many fields such as medicine, the robotic technology, the micro devices, and the sensor technology because they have one important property, "flexibility", that conventional actuators made from metals or ceramics have never had. The actuators based on polymer electrolyte membranes have been investigated actively because these actuators do not need any organic reagents, acid, base, or other specific substances for the actuation, compared with other actuator devices that are based on the conducting polymers or the polymer gels. It has been reported that the polymer electrolyte membranes covered with metallic gold bend toward the anode in response to electrical stimulus in an aqueous solution. This bending behavior is caused by the concentration gradient of water in the membrane due to its electroosmosis. In the case of actuators based on polymer electrolyte membranes, the performance of actuation is affected by many factors. Although some studies about the counter-ion transferring in the membrane and the species or the condition of metal electrodes have been carried out [1, 2], there are few reports that focus on the polymer electrolyte membrane.

In this study, the novel actuators based on hydrocarbon polymer electrolyte membranes having phosphoric acid groups were fabricated to compare with fluorocarbon polymer-based actuators. PHM-AN (Scheme 1), a copolymer of acid phosphoxyethyl methacrylate (PHM) and acrylonitrile (AN), was synthesized and was coated with gold. In order to clarify the method and to reveal various capabilities, we investigated the factors that affect the actuation by comparing two actuators.



Scheme 1 Synthesis of PHM-AN.

---

* Corresponding author. Tel: +81-3-3238-4250; fax: +81-3-3238-4198; E-mail: m-rikuka@sophia.ac.jp

0379-6779/$ – see front matter
doi:10.1016/j.synthmet.2005.07.141

2. Experimental

2.1. Preparation of the Polymer Electrolyte Membranes

PHM was supplied from Uni-Chemical Co., Ltd. The hydrocarbon polymer electrolyte, PHM-AN, was synthesized by radical copolymerization as follows. A dimethylsulfoxide (DMSO) solution of PHM, AN, and 2,2'-azobis-isobutyronitrile was added dropwise to DMSO at 80 °C, and the mixture was stirred for 24 h. The resulting copolymer was precipitated by pouring the reaction solution into methanol, followed by stirring for 24 h. Then the copolymer was filtered and dried under vacuum. PHM-AN was identified by FT-IR and elemental analysis. The copolymer ratio of PHM-AN (PHM : AN) was 1.00 : 3.61, as determined by ^{1}H-NMR. PHM-AN was dissolved in DMSO and a 5 wt.% solution was cast on a Teflon sheet to obtain free-standing films. The ion-exchange capacity of PHM-AN membrane was 1.67 meq/g, as determined by back-titration.

The Nafion®112, 115, and 117 materials (Du Pont) were pretreated in boiling 3 wt.% hydrogen peroxide and 0.5 M sulfonic acid for 1 h each and rinsed with distilled water. The ion-exchange capacity was 0.91 meq/g and the thickness was 50, 125, and 175 μm, respectively.

2.2. Fabrication of Actuator Devices

Actuator devices based on polymer electrolyte membranes were fabricated as follows [3]. Cation exchange was carried out by immersing polymer electrolyte membranes in an aqueous solution of dichlorophenanthrolinegold (III) chloride ([Au(phen)Cl_2]Cl, [4]) for 24 h at room temperature (r.t.). Subsequently, the membranes were soaked in a sodium sulfite aqueous solution for 6 h at r.t. for hydrocarbon polymer membranes and at 60 °C for fluorocarbon polymer membranes in order to reduce Au cations in the membranes and to deposit metallic gold on the surface of the membranes. PHM-AN, Nafion®112, 115, and 117 membranes were coated with gold using this method.

2.3. Characterization of Composites

The amounts of metallic gold deposited on the surface of polymer electrolyte membranes were evaluated from the change of the weight of gold-polymer electrolyte membrane composites before and after gold coating. The thickness of the gold layer was measured with a scanning electron microscope, SEM (HITACHI, S-4500), and the elemental analysis of gold was carried out using energy dispersive X-ray analysis, EDX (HORIBA, EMAX-5770).

2.4. Measurement of Mechanical Properties of Models

Mechanical properties of the Nafion®115 based models with various thickness of Au layer were measured on a SHIMADZU AUTOGRAPH AGS-1KNA tensile machine at the cross-head speed of 10 mm/min. Actuator models were cut into the size of 1.0 cm × 2.0 cm.

2.5. Evaluation of the Actuation

The actuators were cut into pieces 0.3 cm wide and 4.5 cm long, and these pieces were supported vertically in distilled water at r.t. The bending size and the velocity of actuation were measured. The electric stimulus (10 ~ 1500 mV) was supplied from a potentiostat (ALS, Electrochemical Analyzer Model 660B). Actuator models were immersed in a sodium chloride aqueous solution to exchange sodium from (Na^+) prior to the displacement tests.

3. Result and Discussion

3.1. Characterization of Composites

Figure 1 shows SEM images of the cross sections of a Nafion®115 and PHM-AN based actuators. The white parts represent the Au layer and the others are the polymer electrolyte membrane. It was found that the Au layer had a large interfacial area utilizing penetration and reduction of Au cation. In the case of hydrocarbon polymer electrolyte membranes, a fine Au layer was observed by a similar method. The weight of deposited metallic Au and the thickness of Au layer increased with increasing the penetrated amounts of Au cation. The result of EDX confirmed that the metallic gold existed on the surface of the polymer membrane and dispersed uniformly. Such a fine Au layer could not be obtained by the conventional vacuum deposition method. The energy transfer efficiency and the mechanical properties of actuators fabricated by the vacuum deposition were quite poor, because of the small interfacial area between the membrane and the Au layer. In such a case, the Au layer was easily peeled off from the polymer electrolyte membranes.

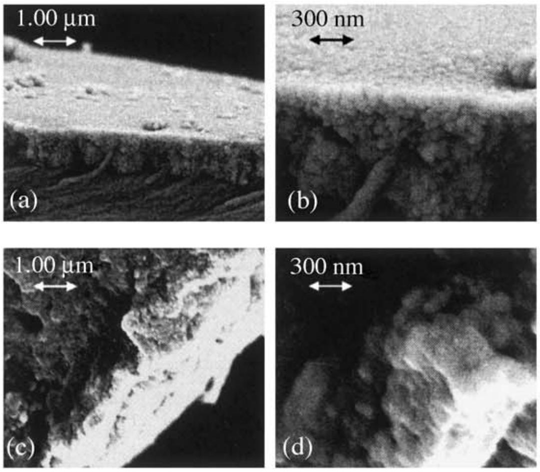


Fig. 1 SEM images of the cross section of Nafion®115 ((a), (b)), and PHM-AN based actuators ((c), (d)).