Solid polymer electrolyte actuator using electrode reaction

Mikio Uchida, Minoru Taya*

Department of Mechanical Engineering, Center for Intelligent Materials and Systems, University of Washington, Box 352600, Seattle, WA 98195-2600, USA

Abstract

A solid polymer electrolyte membrane, Nafion, plated with noble metal is known for the fast bending upon electric field. Since this composite contains water, the applied voltage should be small enough such as 1 V in order to avoid water electrolysis, although its larger deflection demands the higher applied voltage. Nafion with copper–platinum electrodes on its surfaces exhibited larger deflection than that with the pure platinum electrodes upon 1 V. This larger deflection is owing to the electrode reaction of copper that provides larger flux of mobile Cu^{2+}. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Copper–platinum electrode; Nafion; Composite

1. Introduction

Considerable attention has been paid to solid polymer electrolyte–metal composites owing to their promising property as an electrically driven actuator material in the past decade [1–9]. They consist of four components, electrode, solid polymer electrolyte, counter ion and solvent. Perfluorosulfonic acid membrane, Nafion, plated with platinum is typically one of these. The bending of Nafion upon electric field is considered to result from its gradient of the swelling ratio along the electric field (plate thickness) direction. Namely, the hydrated mobile cations are attracted toward the negative electrode side due to the coulomb force by electric field, resulting in the swelling and shrinking at the negative and positive electrode sides of Nafion, respectively, and consequent swelling ratio gradient induces its bending [1,2]. Especially, Nafion–platinum membrane composite has been investigated quite extensively on its bending motion [3], electrode structure [4], surface electrode resistance [5] and electric property [7,8], and its mechanism of motion was theoretically investigated [6,9]. For the sake of using this material as an electrically driven actuator, its larger deflection is preferable which can be achieved by applying higher applied voltage [3]. However, since the solvent of this composite is water, the high voltage creates a problem of the water electrolysis.

Anode reaction : $2H_2O \rightarrow 4H^+ + O_2 \uparrow + 4e^-$

Cathode reaction : $4H_2O + 4e^- \rightarrow 4OH^- + 2H_2 \uparrow$

Neutralization reaction : $4H^+ + 4OH^- \rightarrow 4H_2O$

Total reaction : $2H_2O \rightarrow 2H_2 + O_2 \uparrow$ (1)

In this paper, we show a new electrode system based on a combination of platinum and copper. Although the platinum–copper electrode is not electrochemically stable unlike the noble metals, we can drastically enhance the deflection of the Nafion based on the copper of the platinum–copper electrode. As far as the Nafion with Pt–Cu electrode is to be used under reverse switching mode, the Cu electrode remains stable.

2. Experiment

2.1. Preparation of membrane–electrode composite

Perfluorosulfonic acid membrane, Nafion®117 (Aldrich, Milwaukee, WI) was used as a solid polymer electrolyte specimen. The Pt–Cu metal plating was applied on its surfaces, which serves as the electrode of Nafion. Before the metal plating, the membrane surface was roughened manually by using #2400 sandpaper. Then, both sides of the membrane were chemically plated with platinum, where $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ was used as precursor salts for metallic platinum and $NaBH_4$ as reducing agent [10–12]. Plating was repeated 3 times. Then the Nafion membrane was immersed in 1 M HCl for 1 h followed, by boiling it in the deionized water for 1 h. It was immersed in 0.1 M LiCl

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Table 1
Maximum bending curvature

Specimen	I	II	III	IV
Imported cation	Li^+	Cu^{2+}	Li^+	Cu^{2+}
Electrode	Pt	Pt	Pt–Cu	Pt–Cu
Curvature (mm^{-1})	0.020	0.043	0.057	0.141

or $CuSO_4$ solution over 12 h to introduce cation, Li^+ or Cu^{2+}, into Nafion. After the platinum plating and ion exchange, it was electrochemically plated with copper. The copper plate and Nafion are suspended in the 0.1 M $CuSO_4$ aqueous solution and 3 V of the voltage was applied for 1 min where the distance between them was 3 cm. These plating reactions are given by the following equations:

$$\text{Anode reaction}: Cu \rightarrow Cu^{2+} + 2e^-$$

$$\text{Cathode reaction}: Cu^{2+} + 2e^- \rightarrow Cu \qquad (2)$$
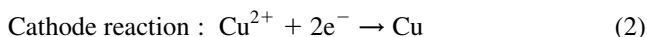
Four kinds of samples were prepared; (1) platinum electrode with lithium mobile cation, (2) platinum electrode with copper mobile cation, (3) platinum–copper electrode with lithium mobile cation and (4) platinum–copper electrode with copper mobile cation. They are designated as specimens I, II, III and IV, Table 1.

2.2. Curvature measurement

Fig. 1 is the illustration of the experimental setup for measurement of bending deformation (curvature). The Nafion specimen was cut into a strip of 2 mm width and 23 mm length, and then it was taken out from the solution and rinsed with deionized water. On measurement in air, surface water left on the strip was wiped away. The Nafion strip was suspended vertically in air. The deformable length was 20 mm, since the edge of 3 mm was clumped to suspend. Its deflection upon applied electric field was recorded using CCD camera and VCR. The coordinate system is used for measurement of its curvature as shown in Fig. 2. From the measured tip position, curvature, ρ, was
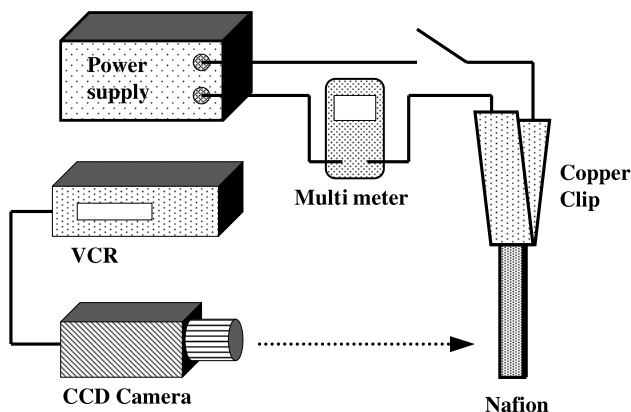

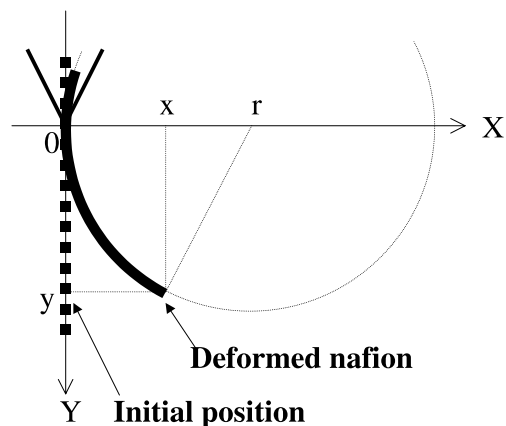Fig. 1. Illustration of experimental setup.

Fig. 2. Definition of coordinate system where the solid and dashed lines represent the deformed and the initial configurations of Nafion, respectively.

calculated by using the following equations:

$$\rho = \frac{1}{r}, \; r = \frac{x^2 + y^2}{2x} \qquad (3)$$

This experiment was conducted in air and deionized water.

3. Results and discussion

Fig. 3 shows the curvature of specimens I and IV as a function of time upon 1 V in air. Fig. 4(a) and (b) show the photographs of the Nafion with Pt electrode and Li^+ cations (specimen I) and that with Pt–Cu electrode and Cu^{2+} cations (specimen IV), respectively. When a specimen was bending, specially in case of specimen IV, it was observed that the surface of the Nafion was drying on anode (shrinking and bending toward side) and water was
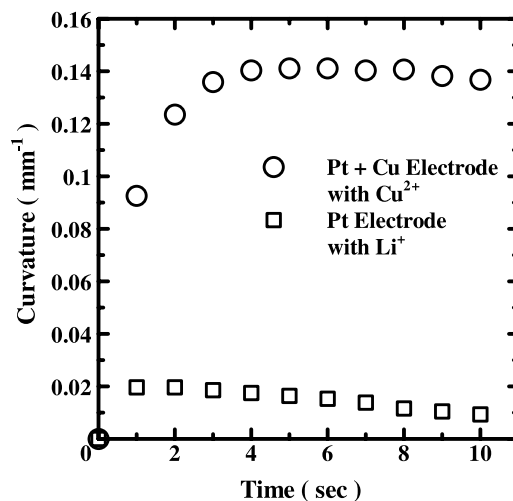

Fig. 3. Time dependence of the curvature of Nafion upon 1 V. Circle: platinum–copper electrode with copper cations, specimen IV. Square: platinum electrode with lithium cations, specimen I.
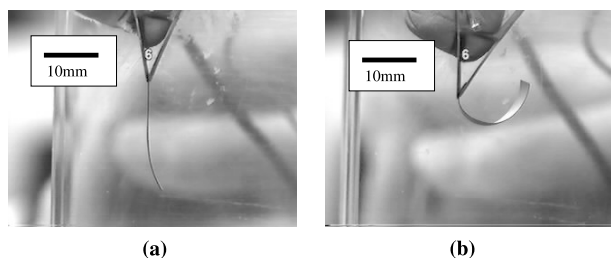
Fig. 4. Maximum bending of Nafion upon 1 V. (a) Platinum electrode with lithium cations, specimen I. (b) Platinum–copper electrode with copper cations, specimen IV.

Fig. 5. Maximum curvature of Nafion with platinum–copper and copper cation (specimen IV) in water vs number of polarity change upon 1 V and each polarity change lasts for 10 s. The positive and negative curvatures correspond to odd and even cycles, respectively.

soaking out of specimen on cathode surface (expanding side), respectively. This indicates that the bending is induced by water transportation in the Nafion. If the bending was induced by electrostatic effect of polymer network, then water squeezing and surface drying should have been observed on shrinking side (anode) and expanding side (cathode) surface, respectively. This also indicates that the plated metal layer was porous. The results of the measured curvatures of all specimens are summarized in Table 1. Specimen IV exhibited the largest curvature among all. It was reported [5] that the Nafion with platinum–copper electrode and lithium cation, specimen III, shows larger force which can be interpreted as larger deflection than that with platinum alone electrode and lithium cation, specimen I. The larger force of specimen III was explained by the increase of surface-electrode conductivity. But the combination of platinum–copper electrode and copper cation, specimen IV, showed remarkably larger deflection than specimen III. This large deflection of specimen IV was not solely due to the increase of electrode conductivity. The difference between specimens III and IV is the cationic species imported as the mobile cations in advance. Thus it is considered that the importation of Cu^{2+} cations plays a significant role in enhancing the bending deflection. However, specimen II did not exhibit such a large deflection despite its having the mobile cations Cu^{2+} in advance. The cause of such a large deflection of the Nafion with Pt–Cu electrode and Cu^{2+} cations, specimen IV, is considered to be due to the close correlation between the imported Cu^{2+} and the copper layer on the Nafion surfaces. In order to clarify this, we performed further deflection tests on the specimens. Since we need to observe the specimen deflection repeatedly to carefully investigate what might be happening, the experiment was conducted in deionized water. Otherwise in air, Nafion would become dry and drying would affects the bending behavior and electrode reaction.

Fig. 5 shows the maximum curvature of specimen IV in water vs the number of polarity change where the applied voltage was 1 V and each cycle lasted for 10 s. The curvature measurement was conducted right after the copper plating. The deflection increases with increase in the number of the polarity change. Other specimens did not exhibit such an incre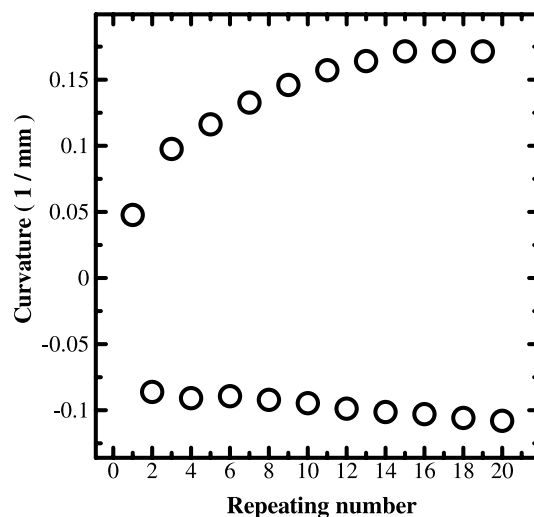ase of the deflection in the deionized water. When the polarity was not changed for a long time, the copper on the surface of anode vanished. This observation implies that the electrode reaction described by Eq. (2) occurred in deed through Nafion. This electrode reaction can occur at 1 V since standard electrode potential of this reaction is 0.34 V. In air, this anode copper vanishing was not observed since electrode reaction is stopped by drying of electrode surface particularly on anode side. Since copper layer was plated after platinum plating, initially, the copper layer of the electrode exists on the platinum layer not directly on the Nafion surface. With the help of Cu^{2+} imported in Nafion in advance and the copper electrode, the electrode reactions are invoked upon applied voltage. Then a copper layer is formed on the outside of platinum and Nafion layer is ionized through porous platinum layer on the anode side and a new copper layer is formed between Nafion and platinum layer on the cathode side. Since the new copper layer is directly in contact with Nafion surface and Nafion has a large amount of the negative charge, $-SO_3^-$, the positively charged additional Cu^{2+} is easily created from the newly formed copper layer upon the applied voltage. Thus the increase of the number of the applying voltage, that is, the repetition of the polarity change, accumulates the amount of copper directly on the Nafion surface, which promotes the Cu^{2+} creation in a accelerated manner. This accumulation of Cu becomes saturated soon as shown in Fig. 5. As explained earlier, the water molecules dragged by the mobile cations in Nafion from the positive side to the negative side induce the deflection. Electrode reaction of copper generates continuous Cu^{2+} flow from anode to cathode, resulting in a larger deflection. This explanation is also in harmony with the smaller deflection of specimen III than specimen IV despite its having copper layer of electrode. Although the difference

in specimens III and IV is the species imported in them as mobile cations alone, the deflections of these specimens are quite different. It is because the combination of the mobile cation Li^+ and the copper layer of the electrode cannot give rise to the cathode electrode reaction. Without the electrode reaction, no additional cation flow is available in Nafion. The large deflection cannot be expected, since Nafion can count only on Li^+ redistribution for its deflection.

To sum up, for the induction of the large deflection of Nafion, the large number of the mobile cations is essential. Such a number of mobile cations is limited by the equivalent weight of membrane. Although it is possible to induce a large deflection by applying a higher electric field as alternative way, this would introduce the electrolysis of water, which is not desired unless the device is always submerged in water. Therefore, using the electrode reaction is a quite effective way to overcome such a dilemma. Increase in mobile Cu^{2+} ions accompanies increase in electron flow, thus the additional Cu^{2+} ions are neutralized with additional $2e^-$. The electrode reaction can continuously create Cu as well as Cu^{2+} at the negative and the positive sides, respectively. Namely, after the Cu^{2+} so created transporting the water molecules from the positive side to the negative side, is terminated, they are degenerated to Cu, and new Cu^{2+} is created, transporting the water molecules. This is a reversible process.

In order to investigate relaxation behavior of bending and repeatability in dry condition, the Nafion specimen was coated by rubber (KRATON, Shell Chemical Company) to minimize the effect of water evaporation from the specimen and then bending was measured in air. Fig. 6 shows curvature change of specimen IV under constant voltage (1 V) and polarity change in air as a function of time, where the polarity was changed every 120 s. It is clear from Fig. 6 that the specimen exhibited the maximum

deflection in about 10 s and then showed gradual relaxation of bending toward the saturated deflection, about a half of maximum deflection. Bending is almost symmetrical on polarity change. Although copper on the electrode moves from one side to the other side by applying voltage, as shown in Eq. (2), this reaction is symmetrical by polarity change. Therefore bending is repeatable by polarity change.

This type of solid polymer electrolyte actuator needs to be in the hydrated state for actuation. Although the Nafion with copper electrode exhibits larger deflection, copper is easily oxidized in wet condition due to its direct exposure to oxygen from surrounding. Namely, additional treatments which avoid drying of Nafion and oxidation of copper are required for use of the Nafion with Cu–Pt electrode for a longer time. Therefore, the surface coating on the composite is essential to avoid both the loss of the solution contained in Nafion and the direct copper exposure to oxygen in the atmosphere. Although non-coated Nafion specimen actuation lasts only for a few minutes at 20°C and 60% humidity condition, we observed that the Nafion coated with butyl rubber film lasts for several days.

4. Conclusion

It was found from the present study that Pt–Cu plated Nafion with mobile Cu^{2+} exhibited much larger deflection than the Nafion with other combinations of electrode and mobile cations. This is attributed to the electrode reaction between the mobile Cu^{2+} and copper layer on the Nafion surfaces, providing more cation flux accompanied by a larger number of water molecules. Since the creation and disappearance of Cu^{2+} continuously occurs owing to the electrode reaction under reverse polarity, Nafion deflection can be induced as if it could make use of the exhaustible Cu^{2+}. Although deflection shows relaxation by time upon constant applied voltage, relaxation is saturated at about a half of maximum deflection. This actuator can be used in air with surface coating to avoid membrane drying.
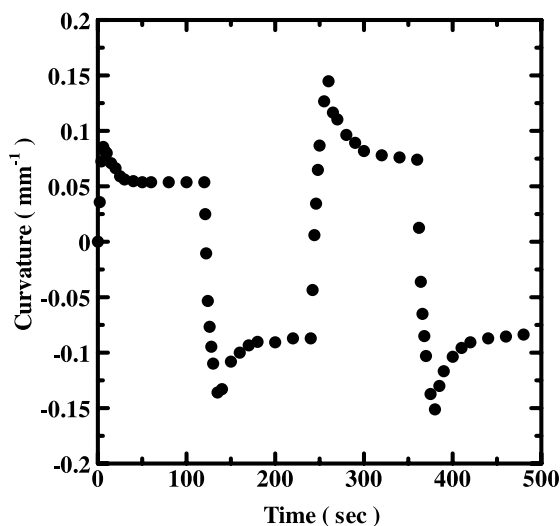
Fig. 6. Curvature change of Nafion with Pt–Cu electrode and copper cation specimen upon applying constant voltage (1 V) and polarity change in air. The polarity was changed every 120 s.

References

[1] Asaka K, Oguro K, Nishimura Y, Mizuhara M, Takenaka H. Polym J 1995;27:436.
[2] Oguro N, Fujisawa K, Asaka K, Onishi S. Sewa. Proc SPIE — Int Soc Opt Engng 1999;3669:64.
[3] Shahinpoor M, Bar-Cohen Y, Simpson JO, Smith J. Smart Mater Struct 1998;7:R15.

[4] Salehpoor K, Shahinpoor M, Razani A. Proc SPIE — Int Soc Opt Engng 1998;3330:50.

[5] Kim KJ, Shahinpoor M. Proc SPIE — Int Soc Opt Engng 1999;3669:308.

[6] Nemat-Nasser S, Li JY. J Appl Phys 2000;87:3321.

[7] Leary S, Bar-Cohen Y. Proc SPIE — Int Soc Opt Engng 1999;3669:81.

[8] Bar-Cohen Y, Shahinpoor M, Harrison JO, Smith J. Proc SPIE — Int Soc Opt Engng 1999;3669:57.

[9] De Genes PG, Okumura K, Shahinpoor M, Kim KJ. Europhys Lett 2000;513:50.

[10] Takenaka H, Torikai E, Kawami Y, Wakabayashi N. Int J Hydrogen Energy 1982;7:397.

[11] Millet P, Pineri M, Durand R. J Appl Electrochem 1989;19:162.

[12] Millet P, Durand R, Dartyge E, Tourillon G, Fontaine A. J Electrochem Soc 1993;140:1373.