

Improved controllability of a fully dehydrated Selemion actuator

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Abstract: Ion exchange polymer membrane in the dehydrated state was found to exhibit bending upon a small applied voltage, although the investigations on the hydrated ion exchange polymer membrane bending behavior have been performed quite intensively for more than a decade for the purpose of producing a practical polymer actuator. Our investigation on the dehydrated ion exchange polymer membrane has revealed that its bending direction is perfectly controllable by the polarity control of applied voltage and the degree of its bending curvature is also almost completely determined by the control of duration time of voltage application on it, while the hydrated ion exchange polymer membranes lack of such properties. Furthermore the longevity of dehydrated ion exchange polymer membrane sustaining such a highly controllable properties has been found quite longer than that of the hydrated ion exchange polymer membrane.

Keywords: Selemion, bending, actuator, hydrated, dehydrated

1. INTRODUCTION

One of ion exchange polymer membranes known as Nafion (Dupont) by the commercial name sandwiched between two thin metal layers exhibits a large bending upon a small applied voltage such as 1V in the hydrated state, where Nafion contains the fixed anions, $-\text{SO}_3^-$, and the free cations, H^+ , in the hydrated state [1-11]. Besides such a low consumption energy and a large bending, its matrix is so soft and bending motion is quite supple, which must be quite beneficial for the purpose of making, for instance, a robot imitating a human like soft motion. Therefore polymer actuator will have a significant contribution to the industrial field and our actual life.

As described above, Nafion in the hydrated state exhibits a large bending upon a small applied voltage, which could lead to the realization of a practical bending mode Nafion actuator. However, there are some problematic issues long hobbling the progress of this kind of polymer actuator researches. Such problems are listed as follows: i) uncontrollability of the Nafion bending direction by the polarity control of applied voltage after its short use, ii) the large deviation of Nafion bending curvature from the desired curvature after its short use, iii) the occurrence of bending relaxation, iv) the short longevity.

One of the ion exchange membranes called Selemion (Asahi Glass Co., Ltd. Japan) (there are two types of Selemion, one is a cation exchange type and another one is an anion exchange type, and here the former one is mainly focused on) sandwiched between two thin metal layers just like Nafion, which contains the fixed anions, $-\text{SO}_3^-$, and free hydrated cations, H^+ , in the hydrated state, also exhibits the bending upon an applied voltage. But it also has the same problematic issues as Nafion has – i), ii), iii), and iv) – in case we use it as a bending mode actuator material. Namely, regardless of ion exchange polymer membranes type, their bending mechanism must be the same and inevitably the same problems are accompanied for the realization of polymer actuator. Recently, the authors of this paper and our collaborator observed the relatively effective bending of largely (not fully) dehydrated ion exchange polymer membrane [12]. Although it has been widely believed that the hydration has a requisite role for the induction bending of ion exchange polymer membrane under the applied voltage, it turned out, in fact, to be absolutely possible to induce the bending of largely dehydrated ion exchange polymer membrane. Although the degree of its bending curvature is

smaller than the hydrated one, still it is a visibly large enough. Our detailed investigation has revealed that the dehydration treatment on ion exchange polymer membrane well overcomes the problematic issues i), ii), iii) and iv).

2. BENDING OF ION EXCHANGE POLYMER MEMBRANE

First of all, the widely accepted bending mechanism of hydrated ion exchange membrane is explained.

2.1. Structure of a bendable ion exchange polymer membrane

As an example, we take up Nafion. Nafion is a sheet type polymer with the thickness of around $180\mu\text{m}$. Fig.1 shows the molecular structure of Nafion. A large number of $-\text{SO}_3\text{H}$ groups are attached to the randomly folding fluorocarbon chains. Fig. 2 is the Nafion sandwiched between two thin metal layers and it contains a large number of $-\text{SO}_3\text{H}$ functional groups. Both surfaces are metal plated and its matrix is hydrated.

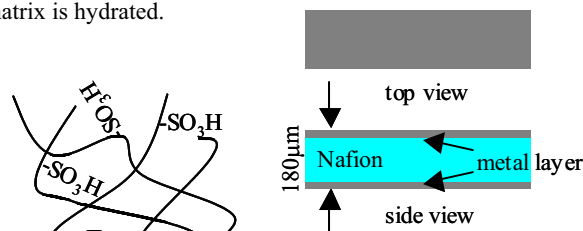


Fig. 1 Structure of Nafion
Main chains are fluorocarbon

Fig. 2 The structure of Nafion sandwiched between two thin metal layers

2.2. Bending mechanism

Application of voltage to Nafion causes its bending. It has been widely believed that the hydrated mobile cations contained in Nafion are dragged toward the top surface side of Nafion by the applied voltage – the top surface of Nafion is connected to the negative terminal of power supply – as depicted in Fig. 3, and it causes the gradient of swelling ratio of Nafion in its thickness direction, then consequently, the bending is induced (see Fig. 3 again).

2.3. Evidences supporting the widely accepted bending mechanism

If the bending mechanism described above is absolutely

right, the ion exchange membrane which contains the free anions and the fixed cations must exhibit the bending in the direction opposite to the bending direction of Nafion, since the hydrated mobile anions contained in that ion exchange polymer membrane is expected to be dragged toward its surface connected to the positive terminal of power supply, then it must consequently cause the bending in the opposite direction as depicted in Fig. 4. Indeed, Nakagawa et al. observed such a phenomenon between the cation exchange type Nafion and the anion exchange type Selemion [7]. Nakagawa et al. forcibly imported CuSO_4 solution into both Nafion and Selemion bodies. Both Nafion and Selemion come to contain both cations, Cu^{2+} , and anions, SO_4^{2-} . However, the free cations, Cu^{2+} , must outnumber the free anions, SO_4^{2-} , in Nafion, while the free anions, SO_4^{2-} , must outnumber the free cations, Cu^{2+} , in Selemion, because Nafion and Selemion contain the fixed anions and cations, respectively, and electroneutrality should be valid in their bodies. Therefore it is expected that Nafion bending is dominated by the hydrated free Cu^{2+} primarily and Selemion bending is dominated by the hydrated free SO_4^{2-} primarily. Thus the bending mechanism described in the section 2.2. predicts that the downward bending of Nafion and upward bending of Selemion. Fig. 5 shows the curvature of Nafion and Selemion, where the bending curvature of Nafion is defined as positive. Since Selemion's curvature in Fig. 5 is negative, Nafion and Selemion exhibit bending in the opposite direction each other as predicted.

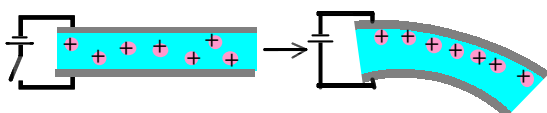


Fig. 3 Bending mechanism of Nafion The shift of hydrated mobile cations toward the top surface direction by the applied electric field results in the gradient of swelling ratio of Nafion along its thickness direction, and it causes the downward bending of Nafion

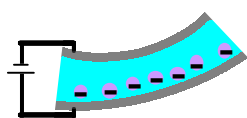


Fig. 4 Bending of the ion exchange polymer membrane caused by the shift of hydrated free anions

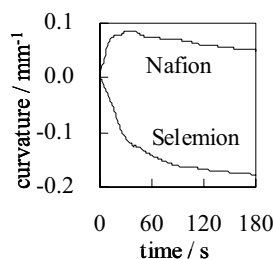


Fig. 5 Time dependence of the curvature of a cation exchange type Nafion and a anion exchange type Selemion swollen with CuSO_4 solution upon 1V

3. EXPERIMENTAL

3.1. Materials

A cation exchange type Selemion was employed as a starting material of a specimen. The functional atomic group contained in this Selemion is $-\text{SO}_3\text{H}$ and it dissociates into $-\text{SO}_3^-$ and H^+ in the hydrated state. For the purpose of comparing the properties of Selemion with those of Nafion which has been long studied in order to produce a bending mode polymer actuator, Nafion was also employed for this study.

3.2. Specimen preparation

Surfaces of Selemion were roughened with a sandpaper. They were plated with silver through the silver mirror reaction [8-10]. Some silver plated Selemions were stored in a 1M HCl solution. This process imports the free ions, H^+ and Cl^- , into the Selemion body, and hereafter called **H-S (Hydrated-Selemion)**. The rest of it was stored in the desiccator for weeks so as to fully dehydrate, and hereafter called **D-S (Dehydrated-Selemion)**.

Nafion was also treated in the same way, and some of it stored in a 1M HCl solution was designated as **H-N (Hydrated-Nafion)**, and the rest of it dehydrated and stored in the desiccator was designated **D-N (Dehydrated-Nafion)**.

3.3. Bending and controllability testing

Bending testing on all four types of specimens, **H-S**, **D-S**, **H-N** and **D-N**, was performed. Constant voltage was imposed on them, and their tip displacement was measured with a laser displacement meter as a function of time. Tip displacement data was converted into the curvature through the simple calculated. Controllability of bending direction and curvature of these specimens are quite important factors for the practical polymer actuators. Therefore we studied these factors through the investigation on the correlation between the bending direction & curvature of specimens and the polarity of applied voltage.

3.4. Oscillation testing

As described above, we had performed the bending testing on all four specimens already, yet it was performed under the constant applied voltage. For the actuator use of ion exchange polymer membrane, it should behave (bend) in perfect agreement with the applied voltage that changes its voltage and polarity for long while. Therefore oscillation testing was performed on all four types of specimens. Their bending curvature was measured as a function of time upon a sine curve type applied voltage.

4. RESULTS AND DISCUSSION

4.1. Bending and controllability testing

Fig. 6 shows the time dependence of **H-N** and **H-S** upon a constant applied voltage, 1 and 3V. In this measurement, a strip of specimen with the size of 20mm-length \times 2mm-width was fixed horizontally and connected to the power supply as depicted in Fig. 3. The bending curvature of specimen in the a downward bending state is defined as a positive curvature, while that of in the upward bending state is defined as a negative curvature. At the initial stage, the higher applied voltage, 3V, causes the larger bending for both specimens, but such a large bending curvature eventually relaxes with time.

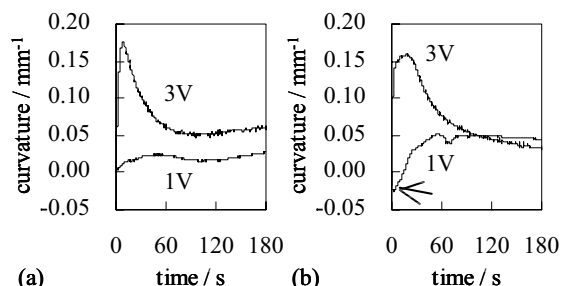


Fig. 6 Time dependence of bending curvature of (a) **H-N** and (b) **H-S** upon constant applied voltage, 1 and 3V

The lower applied voltage, 1V, appears to sustain a fairly constant curvature of them for long while after around $t = 30$ (s). Here we add some comment on the bending curvature behavior of **H-S** upon 1V applied voltage. Right after the impose of 1V on **H-S**, it exhibits upward bending as indicated by an arrow in Fig. 6(b). Although we have yet to identify the cause of it, we strongly speculate that the shift of hydrated anion (primarily hydrated Cl^- in this case) toward the bottom side of **H-S** induced the upward bending at the initial stage of bending – the bottom surface of **H-S** is connected to the positive terminal of power supply –, as long as the conventionally accepted concept on the cause of bending described in the section 2.2 is right.

Next we imposed the voltage, V , regularly changing its polarity – $V = +1V \rightarrow -1V \rightarrow +1V \rightarrow \dots$, $+3V \rightarrow -3V \rightarrow +3V \rightarrow \dots$ – on **H-N** and **H-S**. Fig. 7 shows the results. At the moments indicated by the arrows on the x-axis, the polarity change was given. None of specimens bending direction were well controlled by the polarity change. None of their bending curvatures were well controlled, either, and all of their curvature values decayed with time. Especially in case the applied voltage is the alternation of $+3V$ and $-3V$, neither **H-N** nor **H-S** could recover their curvature to the positive side from the negative side after the first polarity change. It must be caused by the destruction of their matrices by the electrolysis of water contained in them. The applied voltages of 3V as absolute value is so high enough to inevitably cause the vehement electrolysis of water.

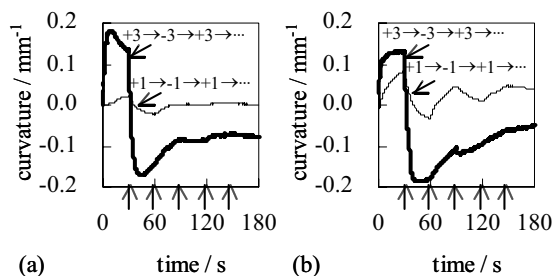


Fig. 7 Time dependence of bending curvature of (a) **H-N** and (b) **H-S** upon 1 and 3V regularly changing their polarity, namely, $+1V \rightarrow -1V \rightarrow +1V \rightarrow \dots$ and $+3V \rightarrow -3V \rightarrow +3V \rightarrow \dots$. Polarity change of applied voltage is given at the moments indicated by the arrows on the x-axis.

Now the same measurements described so far is performed on **D-N** and **D-S**. **D-N** did not exhibit bending upon 1 nor 3V constant applied voltage (no polarity change). **D-S** did not exhibit bending upon 1V constant applied voltage (no polarity change), either, but it exhibited at 3V constant applied voltage (no polarity change) as in Fig. 8. Although its curvature is smaller than the hydrated specimen **H-S**, we observed a good property that no bending relaxation was accompanied. It is quite preferable for the actuator. Furthermore **D-S** bending curvature perfectly follows the polarity change and the curvature value does not decay with time at all as also shown in Fig. 8. Furthermore, the value of bending curvature of **D-S** is well controlled by the duration time of applied voltage. For instance, the curvature indicated by the arrow-A in Fig. 8 is realized 30 seconds after the polarity change indicated by the arrow-a, and the bending curvature value indicated by the arrow-B which is the same as that indicated by the arrow-A is also realized 30 seconds after the polarity change indicated by the arrow-b.

The similar excellent performance was in fact observed about **D-N** in case the higher voltage of 5V (no polarity

change) was applied. But as intuitively understood, the lower consumption energy is better for its practical use. Therefore we did not perform the further investigation on **D-N**, but only the observed time dependence of **D-N** bending curvature upon 5V constant applied voltage is shown in Fig. 9. The bending is actually observed and no bending relaxation is observed unlike the hydrated Nafion, **H-N**. The reason of the higher voltage requirement for the **D-N** bending induction must lie in the thicker matrix of **D-N** than **D-S**. The thicker the specimen thickness, d , becomes, the lower the applied electric field, E , becomes, because E is given by $E = V/d$, where V is an applied voltage. The lower E hardly induces the thicker ion exchange polymer membrane bending.

Judging from the widely accepted bending mechanism described earlier, the creation of mobile

hydrated ions through the hydration of ion exchange polymer membrane is requisite for the induction of bending. However, our research results suggest that the hydration is not in need for the induction of bending and no hydration bring us even better bending performance of ion exchange polymer membrane. No hydration eliminates the bending relaxation and the poor controllability of bending.

Now it is necessary to elucidate what causes the bending of **D-S**. Through the observation of **D-S** bending, we observed the color change of **D-S** surfaces. Always the surface connected to the negative terminal of power supply becomes white color, while the other surface connected to the positive terminal loses white color, and even through the repetitive polarity change, the surface connected to the negative terminal becomes always white and the other surface connected to the positive terminal always loses its white color accordingly. We measured the surface electric conductivity of **D-S** and found the high electric conductivity of the white colored surface and the fading of electric conductivity of the non-white colored surface. So this observation suggests that the white color originates from the color of silver, and the shift of silver layer from one surface to the other surface actually occurs in accordance with the change of polarity of power supply. We can strongly speculate that the shift of silver layer plays a critical role for the induction of **D-S** bending, but we have yet to find out the exact mechanism how it causes the bending. Someone may raise a question that a minute quantity of water remaining in **D-S** must contribute the creation of hydrated mobile ions in **D-S** and consequently

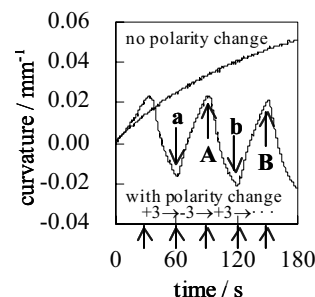


Fig. 8 Time dependence of bending curvature of **D-S** upon the constant (no polarity change) 3V applied voltage and upon 3V applied voltage regularly changing their polarity, namely, $+3V \rightarrow -3V \rightarrow +3V \rightarrow \dots$. Polarity change is given at the moments indicated by the arrows on the x-axis.

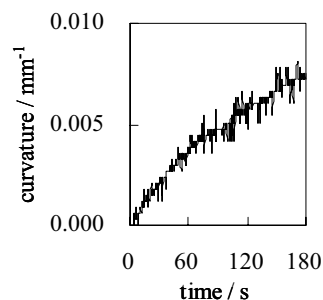


Fig. 9 Time dependence of bending curvature of **D-N** upon a constant applied voltage, 5V

results in its bending. However, we did not observe any gas bubbles generation from **D-S** body under 3V of the applied voltage, when **D-S** is submerged in a silicone oil, where 3V is high enough to cause the electrolysis of water generating H_2 and O_2 gases. Further, we did the following experiment. **D-S** used for a long while under 3V loses its bending ability. Although we have not identified the cause of bending ability loss, actually **D-S** loses its bending ability after long use. Since **D-S** was always used under 3V for long while, we speculated that no water molecules remained in **D-S** body because of the water electrolysis. Dotite (Fujikura Kasei Co., Ltd, Tokyo) which is a mixture of silver powder and an adhesive polymer was spread on this long used **D-S** surfaces, then its bending ability was resurrected. Dotite does not contain any water molecules, therefore the bending of **D-S** is not caused by the existence of minute quantity of water molecules in it. Namely, the supplied silver on **D-S** surfaces from Dotite must have played some role for the induction of **D-S** bending. Therefore silver must have some essential role for the induction of bending.

4.2. Oscillation testing

Actuators should have a long and precise controllability for their practical use. In order to see if **D-S** has such a performance, the alternate voltage of sine curve, whose voltage is, namely, always changing, was imposed on it, and the time dependence of its curvature was measured. For comparison, the same measurements were performed about **H-N** and **H-S**, too. Fig. 10 shows the time dependence of the curvature of **H-N** and **H-S** upon the alternate applied voltages, $V = 1\sin(0.4\pi t)$ (volt) and $3\sin(0.4\pi t)$ (volt), where t is time. Both of them exhibit the oscillation of bending curvature in accordance with the frequency of applied voltage, 0.2 (Hz). However, none of them sustains the same amplitude of bending curvature even for short while. Actually they decay with time soon after the onset of voltage application, while the amplitudes of applied voltages are maintained constant through the course of this experiment. And none of the center of oscillation of bending curvature is maintained constant at 0 (mm^{-1}) even for short while, either. They always largely deviate from 0 (mm^{-1}), although the center of alternate applied voltage is maintained at 0 (mV). On the other hand, the bending curvature amplitude of **D-S** upon the applied voltage, $V = 3\sin(0.4\pi t)$ (volt), is maintained almost constant, and the center of oscillation of bending curvature is maintained constant at 0 (mm^{-1}) for longer while than the others as shown in Fig. 11. Someone may say that the bending curvature of **D-S** is so small compared with those of **H-N** and **H-S** in Fig. 10 and the center of oscillation of **H-N** and **H-S** bending curvature upon $V = 1\sin(0.4\pi t)$ (volt) is fairly close to 0 (mm^{-1}). However, the bending curvature of

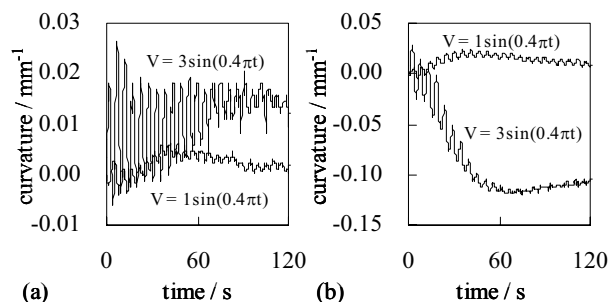


Fig. 10 Time dependence of bending curvature of (a) **H-N** and (b) **H-S** upon the alternate applied voltages, $V = 1\sin(0.4\pi t)$ (volt) and $3\sin(0.4\pi t)$ (volt), where t is time.

D-S is still large enough so that we can detect it with our naked eyes and the bending curvature of **H-N** and **H-S** eventually diminishes toward 0 (mm^{-1}) after a while unlike that of **D-S**, and the deviation of the center of oscillation of bending curvature of **H-N** and **H-S** is quite large compared with that of **D-S** which is almost 0 (mm^{-1}) at any time. Though the amplitude of oscillation of **H-N** and **H-S** bending

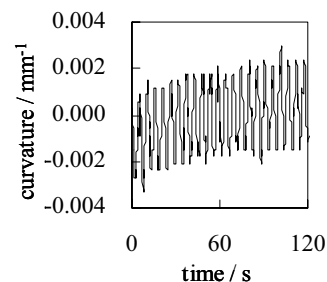


Fig. 11 Time dependence of bending curvature of **D-S** upon the alternate applied voltage, $V = 3\sin(0.4\pi t)$ (volt)

curvature gradually diminishes toward 0 (mm^{-1}) and the center of their oscillation gradually deviates from 0 (mm^{-1}), the fairly regular oscillation of **D-S** bending curvature is sustained even up to $t = 3600$ (s) (the result is not shown, since it is hard to see the detail of bending curvature oscillation from the look of small size diagram). We add that it is true for the dehydrated Nafion, too, although a relatively high applied voltage is in need compared with **D-S** case. Therefore, besides such excellent bending properties of dehydrated ion exchange polymer membranes, they can acquire quite long longevity of bending performance through the dehydration treatment. If the bending is primarily caused by the shift of hydrated mobile ions, such an excellent and long sustainable bending behavior cannot be realized, since water molecules are easily decomposed into H_2 and O_2 through the electrolysis.

Dehydration can let the ion exchange membranes exhibit the better performance, when they are used as the bending mode actuator materials.

5. CONCLUSION

Dehydration of Selemion was found to be an efficient method resulting in the precisely controllable bending of it with a longer longevity. The same was true for Nafion, too, and it let us speculate that any dehydrated ion exchange polymer membranes can be bent precisely at our will for a long period. Dehydration could become a new principle to realize a practical ion exchange polymer membrane actuator.

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