Charge quantity as a sole factor quantitatively governing curvature of Selemion

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Abstract

It was reported previously that the curvature of largely dehydrated silver-plated Selemion had a quantitatively direct correlation to the charge given to it, as long as the redox reaction of silver layers was induced. It was interpreted such that the control of charge quantity given to Selemion led to the precise control of its bending curvature, which was a quite preferable characteristic for the actuator. On the other hand, it was found previously that the curvature of Selemion was largely influenced by the environmental humidity. Therefore, such a quantitative correlation between the charge quantity and curvature might change once the environmental humidity changes. This paper discusses the limits of validity of this correlation. We derived a conclusion that the Selemion curvature was solely governed by the charge quantity, despite the occurrence of significant alteration of Selemion's electric property in accordance with environmental humidity change. Based on this conclusion, we further proposed a mathematical model which related the charge quantity with the Selemion bending curvature.
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1. Introduction

Fabricating a practical polymer actuator has been an attractive theme these years [1–13]. Ion exchange polymer membranes have been regarded as a promising polymer material for fabricating the bending mode actuators. For instance, it was found that one of ion exchange polymer membranes called Nafion (DuPont) exhibited bending upon a small applied voltage, when it was sandwiched by thin metal layers and in the hydrated state [2–6,9–10,13]. Later, other types of ion exchange polymer membranes were found to exhibit large bending, too [10,12]. Among them, we have studied the bending characteristics especially of Selemion (Asahi glass Co. Ltd., Japan) [14–18].

Largely dehydrated silver-plated Selemion exhibits precisely controllable bending behavior under applied voltage [14,17,18]. Previously, we found that its bending curvature was quantitatively governed by the charge quantity given to it, as long as the redox reaction of silver layers on the Selemion sur-

faces was induced [17,18]. It was interpreted such that the application of quantitatively controlled charge to Selemion resulted in its quantitatively controllable bending curvature. It is a quite preferable characteristic for the purpose of employing Selemion as an electrically controllable polymer actuator material.

For the precise control of Selemion bending, the large dehydration (not complete dehydration) treatment to Selemion is necessarily employed. Only a minute quantity of water is essential to be retained in Selemion [17,18], contrary to our conventional treatment that the ion exchange membrane should be largely hydrated for this sort of experiment. However, we reported that such a largely dehydrated Selemion bending curvature was quite susceptible to the environmental humidity [15]. A practical actuator should not be largely influenced by the environmental conditions, otherwise it will results in an improper operation.

This paper addresses the limits of validity of quantitative correlation between the Selemion curvature and the quantity of charge given to it under the influence of environmental humidity change and discusses if the Selemion bending is precisely controllable under the varying humidity conditions.

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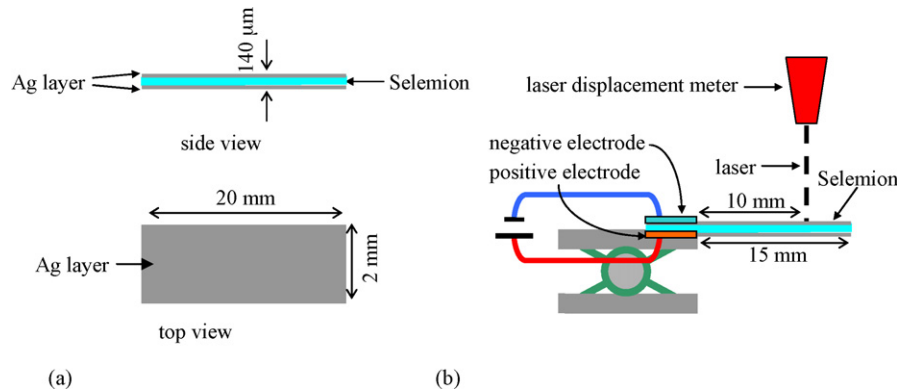*E-mail address:* tmgwhrhs@gifu-u.ac.jp (H. Tamagawa).

Fig. 1. (a) Structure of specimen. (b) Experimental setup for measuring the Selemion tip displacement.

2. Specimen preparation

The surfaces of Selemion containing –SO_3H groups, with a thickness of 140 μm, were roughened with sandpaper. The surfaces were plated with silver by the silver mirror reaction, where the plating procedure is detailed in ref. [11]. It was washed with water and stored in a desiccator so as to be dehydrated.

3. Measurements

The curvature of Selemion was measured by the following procedure. Before starting measurement, Selemion was cut into strips with a dimension of 20 mm × 2 mm × 140 μm (Fig. 1(a)). This strip shape Selemion was left in the air of well controlled humidity for a few hours so that it could absorb a minute quantity of water from the air. After the completion of water absorption, this Selemion strip was horizontally clamped with electrodes as illustrated in Fig. 1(b), where the top and bottom electrodes were designated as negative and positive electrodes, respectively. Upon a given voltage, the tip displacement of Selemion was measured as a function of time with a laser displacement meter. The tip displacement data was converted into the curvature by the same computational procedure as employed in ref. [11].

4. Result and discussion

In order to see if the bending curvature of Selemion was controllable by the charge quantity given to it under varying environmental humidity conditions, we measured the time dependence of Selemion curvature, current and charge, in the air with humidity 70, 80 and 90% upon the applied voltage.

4.1. Occurrence of Ag redox reaction

As touched upon earlier, the predominance of charge quantity to the bending curvature of Selemion emerges, only when the redox reaction of silver layers on the Selemion surfaces is induced. Before making measurement of Selemion curvature, it was necessary to determine the voltage in need for the induction of redox reaction of silver. Firstly, current (I), bending curvature (C) and charge (Q) of Selemion were measured under the applied

voltage (V) increasing from 0 to 1200 mV at a rate of 15 mV s^{-1} by the power supply in the air with the humidity (H) of 70, 80 and 90%. Fig. 2 shows V versus I, where I was obtained as the current per 1 mm-width of Selemion strip. Namely, the measured data of current was divided by the width of Selemion strip. I decreased with a decrease of H. This trend must be caused by the decrease of ion concentration in the Selemion due to the decrease of water contained in Selemion, resulting in a decrease in charge flow rate. Namely, the electric property of Selemion was altered with the change of humidity. However, an abrupt increase of I was observed around at $V = 700$ mV irrespective of H. At the same time, the surface of the Selemion strip connected to the positive electrode blackened around $V = 700$ mV, irrespective of H. The blackened surface suggests the creation of Ag$_2$O by the reaction of $2Ag + (1/2)O_2 \rightarrow Ag_2O$ [15,16]. Once the polarity of 700 mV applied voltage was reversed, the blackened surface returned to the original white surface. The reoccurrence white surface suggests the creation of Ag by the reaction $Ag_2O \rightarrow 2Ag + (1/2)O_2$. These observations strongly suggest that the silver redox reaction started occurring around $V = 700$ mV.

4.2. Correlation of charge versus curvature

At $H = 90\%$, the charge (Q) dependence of curvature (C) of Selemion was obtained under a constant V value of 1000, 1100 and 1200 mV, that was above the voltage at which the redox
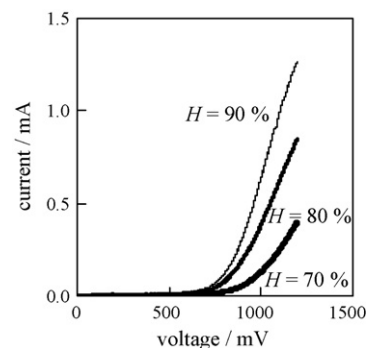

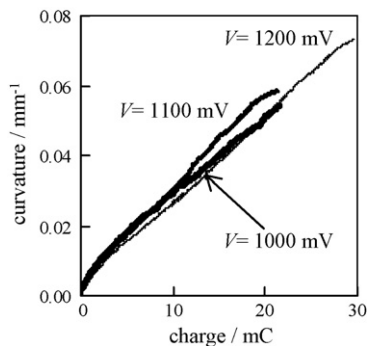Fig. 2. Voltage vs. current of Selemion in the air of humidity $H = 70$, 80 and 90%.

Fig. 3. Charge vs. curvature of Selemion under a constant applied voltage of $V = 1000$, 1100 and 1200 mV.

reaction started occurring. Q was calculated by the numerical computation from $Q = \int I \, dt$. Fig. 3 shows Q versus C, and irrespective of the applied voltage, all curves fall on the almost same linear line. It is interpreted as the curvature C is governed by the charge Q. It is a quite useful property for the actuator, since the curvature is precisely controllable merely by the control of charge. However, such a simple correlation might break down, if the environmental humidity changes. Such a concern was brought up due to the experimental fact that at least the electric property was heavily influenced by the humidity as seen in Fig. 2. Fig. 4 shows the influence of humidity on the curvature of Selemion investigated under a constant V of 1000 mV. All curves fall on the almost same linear line irrespective of humidity, although the electric property of Selemion was largely altered in accordance with the humidity. With this result in mind along with the result given in Fig. 3, we can derive the conclusion that the curvature of largely dehydrated silver-plated Selemion is governed purely by the quantity of charge.

Previously, we proposed a bending mechanism of Selemion [16]. That bending mechanism rests on the creation and loss of Ag and Ag_2O on the Selemion surfaces by the redox reaction of $2Ag + (1/2)O_2 = Ag_2O$. Now, we discuss if our experimental observation so far shown agrees with that bending mechanism.

Firstly, we consider solely the redox reaction of Ag and Ag_2O. The quantity of Ag and Ag_2O created and vanished by the redox reaction has a quantitatively direct correlation to the charge quantity. For instance, the creation of Ag is represented by $Ag^+ + e^- \rightarrow Ag$. Namely, the creation of one Ag atom takes
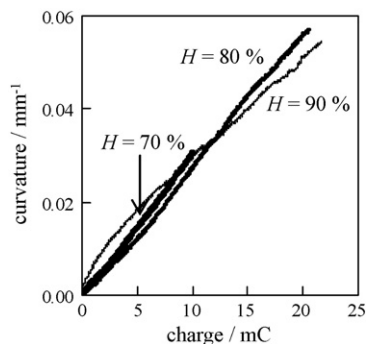

Fig. 4. Charge vs. curvature of Selemion under a constant applied voltage of 1000 mV in the air of humidity $H = 70$, 80 and 90%.

one electron exactly. Therefore, the quantity of charge is directly associated with the quantity of Ag and Ag_2O created and vanished, as long as the whole charge flowing through the Selemion body is involved in the silver redox reaction.

The conclusion we derived earlier in this paper is that what determines the Selemion curvature is merely the quantity of charge. Since the quantity of charge is translated into the quantity of Ag and Ag_2O created and vanished as described here, it is concluded that the quantity of Ag and Ag_2O created and vanished determines the Selemion curvature. This conclusion agrees with the bending mechanism we proposed previously, since that bending mechanism claims that the Ag and Ag_2O creation and loss cause the Selemion bending [16].

How the quantity of Ag and Ag_2O created and vanished determines the Selemion curvature is detailed in the next section, too.

4.3. Bending mechanism of Selemion

Prior to explaining the bending mechanism of Selemion we proposed previously, we would like to show the widely accepted existing bending mechanism for the commonly studied ion exchange polymer membranes as below.

One of ion exchange polymer membranes, called Nafion, exhibits bending upon an applied voltage, when it is sandwiched by two thin metal layers just like Selemion illustrated in Fig. 1 and highly hydrated. Although the bending mechanism of Nafion has not been completely elucidated yet, it has been widely believed that the shift of hydrated ions contained in Nafion causes its bending [16]. Once the voltage is applied to Nafion, the hydrated mobile ions inside Nafion are dragged toward one side, and such an ions shift generates the volume gradient in the thickness direction, resulting in the bending (Fig. 5(a)). However, at the same time, it is believed that the backward flow of water molecules occurs, causing the bending relaxation (Fig. 5(b)) [16]. This bending mechanism cannot explain the bending of Selemion, since Selemion never exhibits the bending relaxation.

Now, we explain the bending mechanism of Selemion we proposed previously [16]. Selemion bends in the positive electrode direction. Whenever the Selemion was bent, we observed the occurrence of the following reactions $2Ag + (1/2)O_2 \rightarrow Ag_2O$ and $Ag_2O \rightarrow 2Ag + (1/2)O_2$ at the Selemion surfaces which were connected to the positive and negative electrodes, respectively [16]. First, we focus on the reaction $2Ag + (1/2)O_2 \rightarrow Ag_2O$ occurring at the Selemion surface connected to the positive electrode. The surface of Selemion is quite roughly concave and is coated with silver atoms as illustrated in Fig. 6(a). When the oxidation reaction is induced at the surface connected to the positive electrode, silver atoms associate with one another through the intermediary of an oxygen atom to form Ag_2O. Formation of Ag_2O narrows the neighboring surfaces of Selemion, surface-α and surface-β, which are illustrated in Fig. 6(b), causing the gap narrowing. At the Selemion surface connected to the negative electrode, the opposite phenomenon must be induced, that is the gap widening by the reaction $Ag_2O \rightarrow 2Ag + (1/2)O_2$. Consequently, the redox reac-
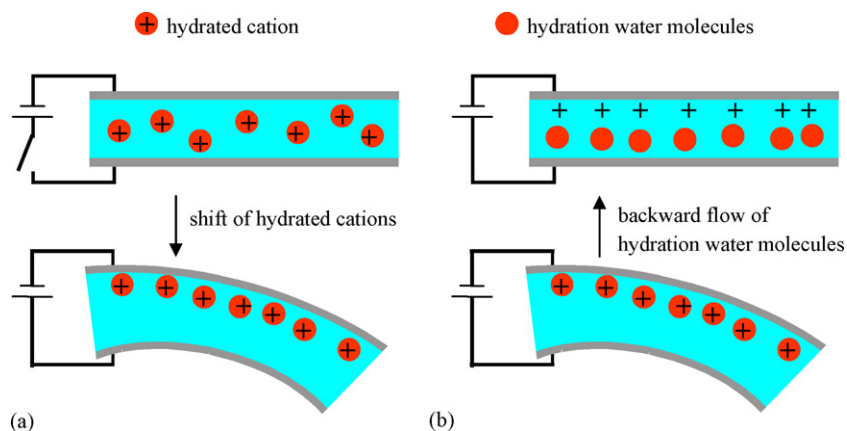
Fig. 5. (a) The bending of Nafion caused by the volume gradient in its thickness direction due to the shift of hydrated mobile ions. (b) The bending relaxation of Nafion due to the backward flow of hydration water molecules.

tion results in the bending of Selemion in the direction of positive electrode. This bending mechanism describes that the bending curvature of Selemion is directly related to the quantity of Ag and Ag_2O created and vanished, in other words the quantity of charge. Next, we propose a mathematical model of Selemion bending which associates the curvature with the quantity of Ag and Ag_2O created and vanished (or quantity of charge).

4.4. Mathematical model of Selemion bending

It is assumed that the angle δ is generated by the onetime reactions $2Ag + (1/2)O_2 \rightarrow Ag_2O$ and $Ag_2O \rightarrow 2Ag + (1/2)O_2$ which occurred on the Selemion surfaces at the right end of electrodes – the original point "o" – as illustrated in Fig. 7 (see Fig. 1(b) as well). Namely, it is assumed that the one-time redox reaction corresponds to the generation of angle δ. Actual bending phenomenon is accompanied by a number of redox reactions. Therefore, we assume the uniform distribution of onetime redox reactions at N individual positions ($N \gg 1$) on the Selemion surfaces which produces the bending of Selemion as illustrated in Fig. 8(a). Selemion bends, since the angle δ is formed at individual redox reaction positions as illustrated in Fig. 8(a). Since N is an extremely large number, we can regard the thick solid line representing Selemion illustrated in

Fig. 8(a) as a smooth curve in a macroscopic view represented by the dashed thick line as illustrated in Fig. 8(b). Defining angle θ brings θ/N (=2δ) as the central angle of individual sector form as illustrated in Fig. 8(b). In this case, the curvature of Selemion, ρ_N, is given by $\rho_N = 1/r_N = [(\theta/N) \times N]/L = \theta/L$, where r_N is the curvature radius and L is the length of Selemion from the original point "o" to the free end. If totally $2N$ redox reactions occurs at $2N$ positions on the Selemion surfaces, ρ_{2N} is given by $\rho_{2N} = 1/r_{2N} = [(\theta/N) \times 2N]/L = 2(\theta/L) = 2\rho_N$. This model is extended to the occurrence of nN reactions at nN positions on the Selemion strip, and ρ_{nN} is given by $\rho_{nN} = 1/r_{nN} = [(\theta/N) \times nN]/L = n(\theta/L) = n\rho_N \propto n$ ($\rho_N = $ constant) $\propto nN$ ($N = $ constant). This equation is interpreted in a way that the curvature, ρ_{nN}, is proportional to the number of reactions, nN, in other words, the number of Ag and Ag_2O creation and loss or the number of charge involved in this reaction. This conclusion agrees with our experimental observations
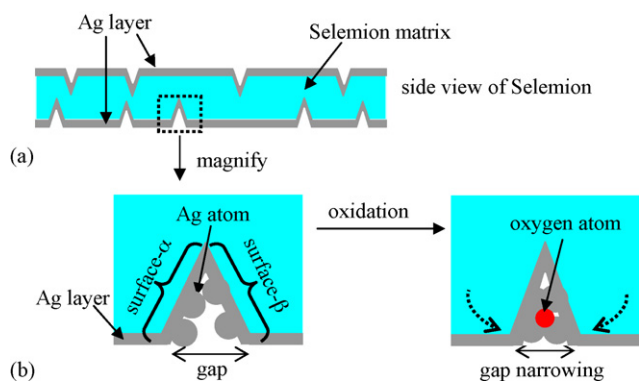

(a)

(b)

Fig. 6. Bending mechanism of Selemion. (a) Surface structure of Selemion. (b) Gap narrowing at the concave point of Selemion surface by the oxidation of silver atoms.
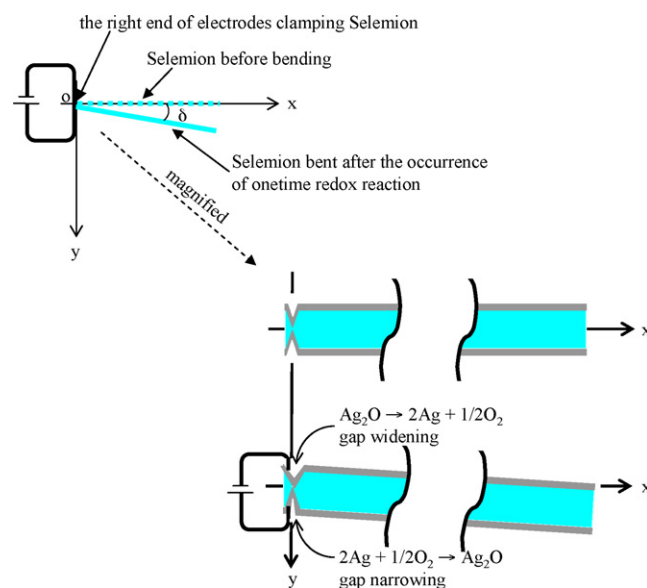

Fig. 7. Mathematical model of Selemion bending with the coordinate system, where the original point "o" is defined as the right end of electrodes clamping Selemion. Onetime reduction and oxidation reactions occur at the top and bottom surfaces of Selemion, respectively, at "o".
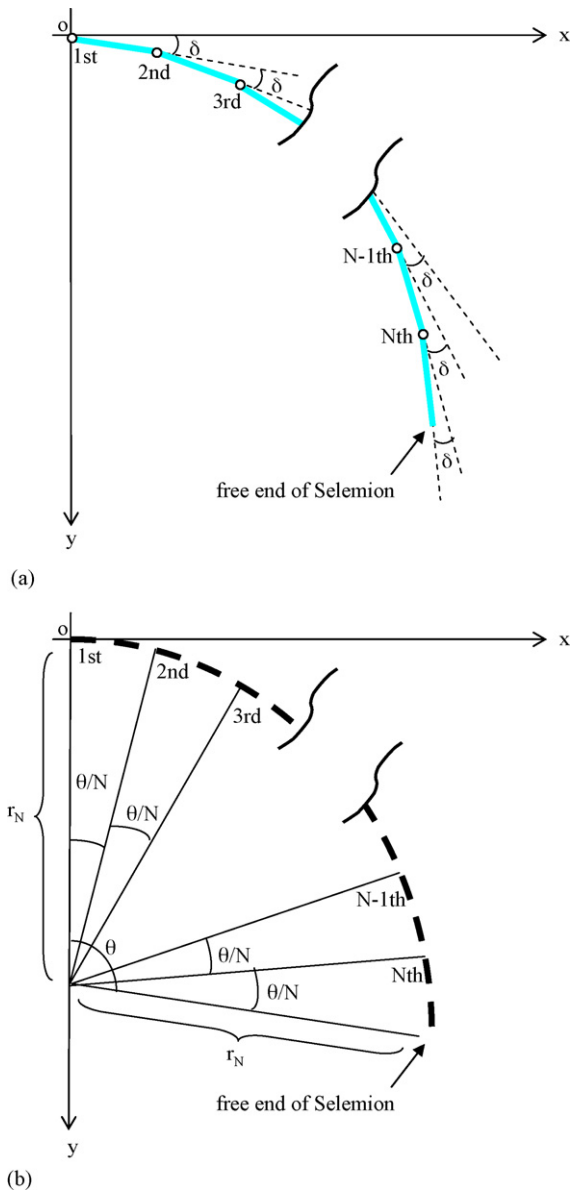
Fig. 8. (a) Mathematical model of Selemion bending, when the onetime redox reaction occurs at N positions on the Selemion surfaces at the regular interval. (b) Central angle, θ, formed by onetime redox reaction occurring at individual N positions.

shown in Figs. 3 and 4. Furthermore, the occurrence of no bending relaxation of Selemion, which is touched upon in Section 4.3, can be well explained by this mathematical model, since this model describes that the bending phenomenon necessarily accompanies the redox reaction induced by the applied voltage. Without the induction of redox reaction, Selemion can exhibit neither bending relaxation nor normal bending.

5. Conclusion

It was found that the Selemion curvature was solely governed by the charge quantity induced, even though the Selemion's electric property changed largely in accordance with the environmental humidity. Therefore, we believe that merely the control

of charge quantity can lead to the precise control of Selemion bending curvature. Based on this finding that the curvature has a quantitative dependence on the quantity of charge, we could put forward a quantitative mathematical model associating the Selemion bending curvature with the quantity of charge.

Acknowledgment

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