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# Preparation of Gold−Solid Polymer Electrolyte Composites As Electric Stimuli-Responsive Materials

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The construction of an electromechanical actuator with large displacement, with fast time response, and without electrolytic gas evolution in pure water or saline is described. Improvement in the previously reported platinum−polymer electrolyte membrane composite was made by switching to gold, deposited by the “impregnation−reduction method”, using cationic gold complexes and reducing agents. The gold-composite actuator showed larger displacements than the platinum composite at the same voltage and at lower loading. In addition, no gas evolution occurred up to the maximum applied voltage [>2.0 V], due to the much higher overvoltage for hydrogen and oxygen evolution on gold.

## Introduction

There is an increasing interest in a “chemomechanical system”, which converts chemical energy into mechanical energy, for its application to an actuating device which behaves like artificial muscle. Most success to date has been made with electrically stimulated “chemomechanics”. For example, Osada et al. have reported that films of a negatively charged polymer gel, such as poly(2-acrylamido-2-methyl propane)sulfonic acid and surfactant counterions may be induced to bend toward the anode under polarization due to electrophoretic charge redistribution.[1,2] Elsewhere, Kaneto described an alternative type of electromechanical actuator based on expansion and contraction of polyaniline thin films due to reversible redox chemistry with hydrogen.[3]

In our previous work,[4−6] it was found that the composite of a proton exchange membrane (PEM) with platinum electrodes bent toward the anode in aqueous solution. It is believed that the bending mechanism is due primarily to establishment of a water concentration gradient caused by electroosmosis. This actuating device shows quite rapid response to electric stimuli (within 100 ms for reaching maximum displacement) in pure water or saline. Its application to several robotic actuators has also been described.[7] Displacement is almost proportional to the applied voltage below 1.7 V, but water electrolysis occurs on the platinum electrodes beyond this threshold voltage, which is seriously undesirable for potential in vivo use. The ideal actuator should show large displacement, good time response, and high durability, without gas evolution. Gold is the most promising candidate as an alternative electrode due to its high overpotential for hydrogen and oxygen evolution.[8] Gold may offer other advantages in terms of softness, nontoxicity, and high electric conductivity.

Metal/PEM composites have been given much attention because of their established use in several processes, such as water electrolysis, fuel cells, electroorganic synthesis, and sensors. Two different plating methods, known as “reductant permeation” (RP) and “impregnation−reduction” (IR), have been successfully developed for direct contacting of a polymer electrolyte membrane and metal electrodes under wet conditions. In the RP method, developed by Takenaka and Torikai,[9,10] a metal layer is formed on the surface of a membrane by permeation of reducing agents into the other side of the membrane when a metal complex solution (e.g., $H_2PtCl_6$, $RuCl_3$) and a reducing solution (e.g., $NaBH_4$, $NH_2NH_2$) placed on both sides of the membrane, respectively. In the IR method, the cation exchange membrane with preexchanged cationic metal species e.g., $[Pt(NH_3)_4]^{2+}$, is subsequently immersed in the reducing solution, which reduces and displaces the metal toward the outer surfaces of the membrane.[11,12]

For optimum performance, the metal-plating step should satisfy the criteria listed below. It should yield metal particles deposited at, or very close to, the membrane surface; it should have a large interfacial area between metal particles and the membrane to

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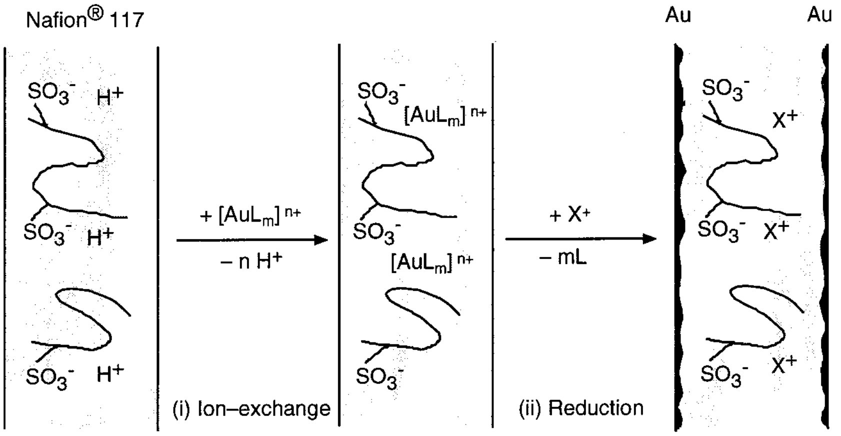

**Figure 1.** Schematic representation of the gold–solid polymer electrolyte composite prepared by the impregnation–reduction method: (i) the ion-exchange step and (ii) the reduction step.

maximize both the electrochemically active surface area and adhesion; and sufficient metal interparticle contact for low electrical resistance. The IR method is known to best achieve these criteria.[13] Indeed, it is the basis for the fabrication of the Pt/PEM actuator described above, as well as membrane electrode assemblies for water electrolyzers[14–17] and sensor devices.[18–20]

To date, however, only the RP method has been reported for the preparation of gold/PEM composites, due primarily to the difficulty of finding cationic gold complexes which are stable in aqueous solution.[21–26] In this laboratory, the use of cationic gold complexes with organic chelate ligands for depositing gold by the IR method have recently been patented.[27–29] Here, we describe a novel IR method for the preparation of gold/PEM composites and their application to electric stimuli-responsive actuators. In this work, (dichloro)(phenanthroline)gold(III) chloride ($[Au(phen)Cl_2]Cl$) and bis(ethylenediamine)gold(III) chloride ($[Au(en)_2]Cl_3$) were chosen as suitable gold precursors, and synthesized in house.

## Experimental Section

**Preparation of the Composites.** Figure 1 is a schematic representation of the IR method for preparation of a gold–Nafion composite. Gold loading was performed on Nafion 117 (Du Pont), which is a typical perfluorocarbon sulfonic acid cation-exchange membrane with an ion-exchange capacity of $0.909 \times 10^{-3}$ equiv $g^{-1}$ and 180 $\mu$m thickness in the dry state. Dichlorophenanthrolinegold(III) chloride ($[Au(phen)Cl_2]Cl$) and bis(ethylenediamine)gold(III) chloride ($[Au(en)_2]Cl_3$) were synthesized according to the literature.[30,31] Cation exchange (impregnation) was carried out by immersing the $H^+$ form of the Nafion in aqueous solutions ($10^{-3}$ to $10^{-2}$ M) of these gold complexes overnight at room temperature (Figure 1(i)). The membrane was washed with water to remove the excess metal species. Subsequently, the membrane was immersed in reducing solution ($10^{-3}$ to$10^{-2}$ M) at 40–60 °C for 5 h to precipitate metallic gold (Figure 1(ii)). Sodium borohydride ($NaBH_4$), sodium L-ascorbate (Na-asc), sodium sulfite ($Na_2SO_3$), and dimethylamine borane (DMAB) were used as reducing agents.

**Ion-Exchange and Permeation Behavior in the Solid Polymer Electrolyte Membrane.** While a Nafion membrane was immersed in aqueous solution containing cationic species, such as $[Au(phen)Cl_2]^+$ and $[Au(en)_2]^{3+}$ at 25 °C with constant stirring, a certain volume of the solution was taken for elemental analysis with an inductively coupled argon plasma atomic emission spectrometer, ICP (Nippon Jarrell-Ash, ICAP-575 II). The incorporated amount of gold complexes in the membrane was determined from the concentration change in the solution.

The permeation behavior of reducing agents in the membrane was investigated by the following method. A Nafion membrane (1.77 $cm^2$) was mounted in a two-compartment cell. The left-hand compartment was filled with a 1 M reducing solution and the right-hand compartment was filled with pure water. A certain volume of the solution was taken from the right compartment for analysis. ICP was used for determining the concentration of boron in $NaBH_4$ or DMAB, or carbon in Na-asc. Quantitative analysis of sulfite, $SO_3^{2-}$, was carried out by UV spectrometry as described elsewhere.[32,33] The concentration of $SO_3^{2-}$ in the right compartment was determined from the absorbance of Hg(II)/$SO_3^{2-}$ complexes at 250 nm obtained by UV–vis spectrometer (Hitachi, U-2000) after adding $10^{-2}$ M $Hg(NO_3)_2$ and 1 M $H_2SO_4$ aqueous solution.

**Characterization of Gold Layers of the Composites.** The prepared composites were examined with a scanning electron microscope, SEM (Hitachi, S-2500), and the distribution of gold layers was analyzed by an energy-dispersive spectrometer, EDS (Horiba, EMAX-3700). The thickness of gold layers was estimated with a fluorescent X-ray coating thickness gauge (Seiko Instruments & Electronics Ltd., SFT-157) with correction for the fluorescent X-ray intensity emitted

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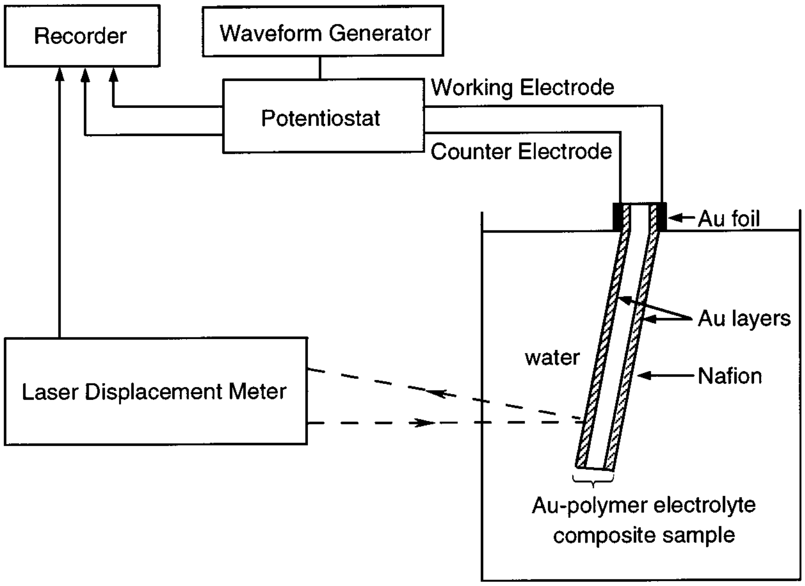

**Figure 2.** A schematic drawing of displacement measuring system.

by another gold layer attached on the backside. The specific resistance of loaded gold layers of ring-shaped specimens in 20 mm diameter was determined with a LCR meter (Yokogawa-Hewlett-Packard 4262A).

**Evaluation of the Performance of the Composite as an Actuator Device.** Figure 2 illustrates the apparatus for measuring displacement of the prepared gold/PEM composite. This was cut into a ribbon (1 mm wide and 12 mm long) and supported vertically in water by clamping with gold foil to ensure electrical contact to the plated gold surfaces. The plated gold layers were used as the working electrode and counter electrode, respectively, while the counter electrode also served as reference. A square-wave voltage was supplied from a waveform generator (Yokogawa AG1200) and a potentiostat/galvanostat (Hokuto Denko HA-501G). Displacement of the free end 8 mm distant from the fixed point was measured by a laser displacement meter (Keyence LC-2220/2100) directed through a glass window of the sample cell at room temperature. All measured values were logged by a digital recorder (Yokogawa ORM1200).

## Results and Discussion

**Preparation of the Gold Composites.** After ion exchange of $H^+$ in the Nafion membrane by gold complexes, the membrane was exposed to various kinds of reducing solutions. The distribution of precipitated gold particles depended on the reduction conditions. Figure 3 shows examples of SEM photographs of the composites cross sections prepared by the reduction of $[Au(phen)Cl_2]^+$ with $NaBH_4$ or DMAB. The gold particles appear in white. With $[Au(phen)Cl_2]^+$ as precursor, $NaBH_4$ and DMAB treatment resulted in double gold layers both under and at the membrane surface, and thick gold layers with low density, respectively. The morphologies of these gold layers were not suitable for use as an actuator, since their electrical conductivities were too low. Milder reducing agents such as Na-asc and $Na_2SO_3$ were found to prevent the internal deposition of gold. Figure 4 shows SEM photographs of good composites. Metallic gold concentration profiles across the membrane analyzed by EDS are represented by the lower traces. Similar gold distributions were obtained for the combination of $[Au(en)_2]^{3+}$ and $NaBH_4$ or Na-asc.

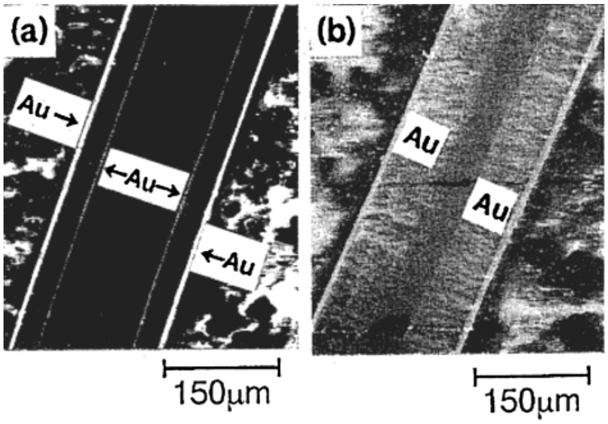

**Figure 3.** SEM photographs of composite cross sections prepared by the reduction of $[Au(phen)Cl_2]^+$ with $NaBH_4$ (a) or DMAB (b) showing internal location and distribution of gold.

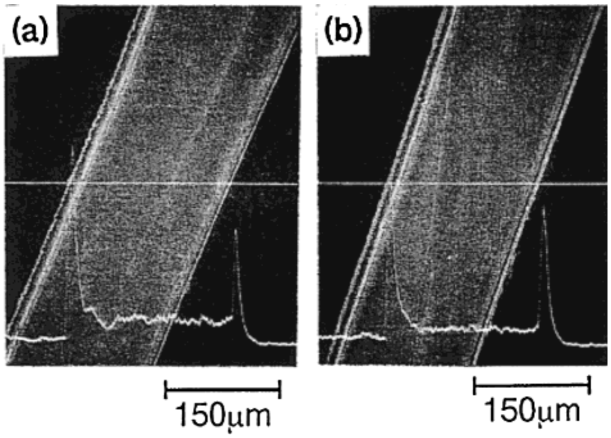

**Figure 4.** SEM photographs of composite cross sections successfully prepared by the reduction of $[Au(phen)Cl_2]^+$ with Na-asc (a) or $Na_2SO_3$ (b). White lines represent gold concentration profiles across the membrane on white straight lines analyzed by EDS.

The mechanism of the ion exchange and precipitation process in the IR method has already been investigated for the preparation of Pt−Nafion composites using $[Pt(NH_3)_4]Cl_2$ and $NaBH_4$.[34,35] The diffusion rate of gold

**Table 1. Appropriate Reducing Conditions and Properties of Gold Layers in Successfully Prepared Composites**

| no. | complex | reductant (concentration) | T, °C | weight, mg cm$^{-2}$ | thickness, $\mu$m | specific resistance, $\Omega$ cm | color |
|---|---|---|---|---|---|---|---|
| 1 | [Au(phen)Cl$_2$]Cl | Na-asc (2 × 10$^{-3}$ M) | 60 | 2.2 | 1.3 | 2 × 10$^{-5}$ | gold |
| 2 | [Au(phen)Cl$_2$]Cl | Na$_2$SO$_3$ (3 × 10$^{-3}$ M) | 60 | 2.2 | 1.4 | 5 × 10$^{-5}$ | gold |
| 3 | [Au(en)$_2$]Cl$_3$ | NaBH$_4$ (9 × 10$^{-3}$ M) | 40 | 0.8 | 0.5 | 2 | black |
| 4 | [Au(en)$_2$]Cl$_3$ | Na-asc (2 × 10$^{-3}$ M) | 60 | 0.8 | 0.5 | 7 × 10$^{-5}$ | gold |

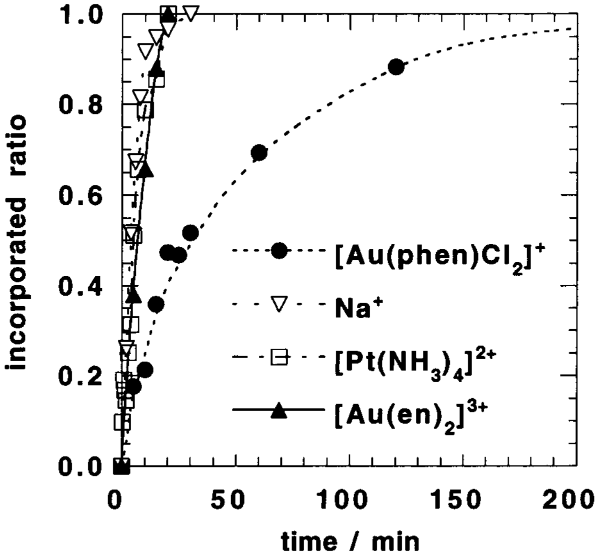

**Figure 5.** Ion-exchange behavior of H$^+$ by cationic species in a Nafion membrane at 25 °C.

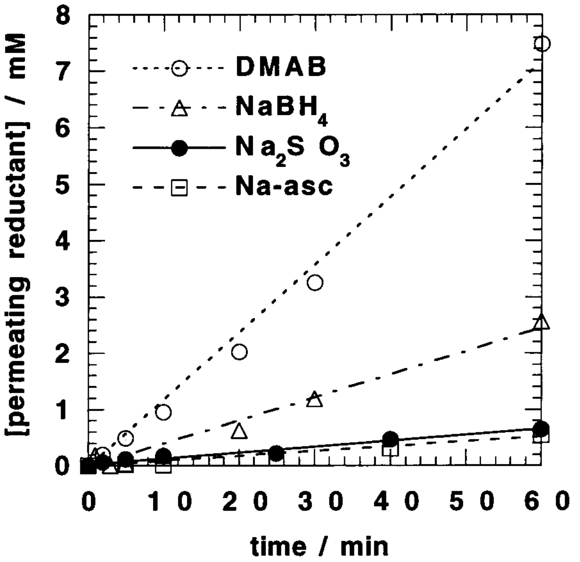

**Figure 6.** The concentration of permeated reducing agents from 1 M aqueous solution through a 1.77 cm$^2$ Nafion membrane, vs time.

complexes, and permeation rate of reducing agents, in the membrane, are considered to be the most relevant. When permeation of a reducing agent is much faster than diffusion of the gold complex, gold is deposited inside the membrane. In contrast, if diffusion of the gold complex is much faster than reductant permeation, gold particles will precipitate in the solution. To form gold layers just on the membrane surface, the respective diffusion rates must be suitably balanced.

Figure 5 shows the ion-exchange behavior at 25 °C of protons in the membrane by gold complexes ([Au(phen)Cl$_2$]$^+$ and [Au(en)$_2$]$^{3+}$), with other cations (Na$^+$ and [Pt(NH$_3$)$_4$]$^{2+}$) included for reference. This shows plots of ratios of incorporated cations to the theoretical amount based on the estimated sulfonate concentration as a function of time. The stoichiometrically incorporated weights in the cationic species were calculated to be 2.3 mg cm$^{-2}$ (Au) for [Au(phen)Cl$_2$]$^+$, 0.76 mg cm$^{-2}$ (Au) for [Au(en)$_2$]$^{3+}$, 0.27 mg cm$^{-2}$ (Na) for Na$^+$, and 1.0 mg cm$^{-2}$ (Pt) for [Pt(NH$_3$)$_4$]$^{2+}$. The ratio of the adsorbed weight of gold was approximately $^1/_3$ for [Au(en)$_2$]$^{3+}$ to [Au(phen)Cl$_2$]$^+$, in which the controlling factor is maintenance of charge balance. According to Figure 5, the incorporation rate of [Au(phen)Cl$_2$]$^+$ was much slower than that of [Au(en)$_2$]$^{3+}$, or small cations such as Na$^+$ and [Pt(NH$_3$)$_4$]$^{2+}$ used for the preparation of the Pt–Nafion composite. It is presumed that steric hindrance of the bulky phenanthroline group by the membrane's fluorocarbon backbone is operative. Such a remarkably small diffusion rate of [Au(phen)Cl$_2$]$^+$ is consistent with the frequently observed internal deposition of gold when using [Au(phen)Cl$_2$]$^+$ as a precursor, in this work.

The permeation behavior of reducing agents is shown in Figure 6, as plots of concentration of reducing agents which permeate into the pure water compartment from a 1 M reductant solution through a 1.77 cm$^2$ Nafion membrane. The permeation rates of DMAB and BH$_4^-$ are much larger than asc$^-$ and SO$_3^{2-}$. Therefore, reducing agents such as DMAB and NaBH$_4$ are likely to cause internal deposition of gold in the case of the [Au(phen)Cl$_2$]$^+$ reduction.

Table 1 summarizes the properties of the gold layers in successfully prepared composites. Appropriate reduction conditions for the formation of suitable gold layers from two gold complexes, and various complex/reductant combinations are shown in the table. Na$_2$SO$_3$ and Na-asc effected the reduction of [Au(phen)Cl$_2$]$^+$ to produce 2.2 mg cm$^{-2}$ (1.3 and 1.4 $\mu$m) gold layers, respectively. On the other hand, 0.8 mg cm$^{-2}$ (0.5 $\mu$m) gold layers were obtained from the reduction of [Au(en)$_2$]$^{3+}$ by NaBH$_4$ and Na-asc. It is estimated that >95% of the incorporated complex was precipitated to gold in these methods.

The resistance and color of the gold surface depended on the reduction conditions. Gold layers in composites nos. 1, 2, and 4 had relatively small resistances, which were around 10 times larger than that of metallic gold foil (2 × 10$^{-6}$ $\Omega$ cm) and were visibly gold. However, the surface resistivity of the composite no. 3, colored black, was very large (2 $\Omega$ cm). Here, it is supposed that the gold particles are extremely finely dispersed with poor electrical contact.

**Performance of the Gold–Solid Polymer Electrolyte Composite Actuator.** Figure 7 shows typical

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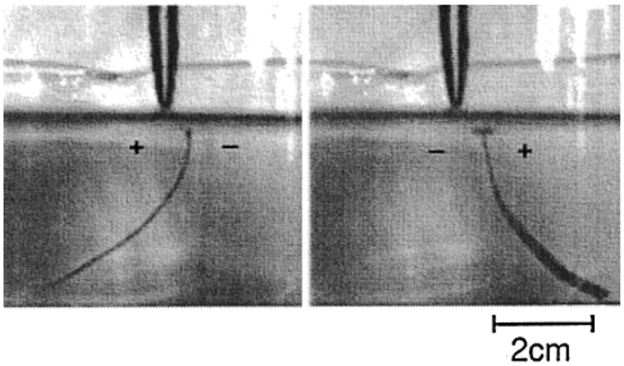

**Figure 7.** Bending effects in the water-immersed actuator composed of the Au−Nafion composite (sample no. 2 in Table 1) driven by a 2.0 V rectangular wave.

bending response of the prepared actuator device (5 mm wide and 50 mm long) with the composite (no. 2 in Table 1), immersed in water at room temperature. Rapid bending toward the anode in response to a 2.0 V rectangular wave was observed without any gas evolution. The bending angle between the tangent to the free end of the ribbon and the vertical reached about 40° in each direction, when the electrical polarity was switched. Similar behavior was observed for actuators from composites nos. 1 and 4. However, composite no. 3 performed poorly due to the poor electrical conductivity of its electrode.

The displacement and current response of the composite (sample no. 2 in Table 1) driven by a 1.8 V rectangular wave are shown in Figure 8. Responding to a step voltage, an ionic current pulse was rapidly created, but decayed quite fast, reminiscent of capacitive charging. The bending response follows the current pulse, in rapidly reaching a maximum deflection to the anode side, and then reversing gradually. In reverse polarity, the response is almost identical. Charging current for making electric double layer induces ion flux and electroosmotic drag of water from the anode to the cathode. The difference of water content in the membrane swells or shrinks the membrane near the cathode or anode, respectively. The slow reverse change back toward the original position responds to the back diffusion of water.

Unlike the previously reported Pt−Nafion actuators,[4−6] which needed about 3 mg $cm^{-2}$ platinum loading by the IR method and electroless plating to perform satisfactorily, these Au−Nafion actuators have lower loadings (0.8−2.0 mg $cm^{-2}$) obtained in a single step. The main benefits of gold over platinum lie in its large conductivity, and its high overvoltage for hydrogen and oxygen evolution in aqueous solution. Furthermore, the conductive layers of the Au−Nafion actuators are more flexible and free from cracking, possibly related to the loading and softness of gold. The performance of the gold/PEM actuator is now being studied intensively with respect to the morphology of the gold layers and how best to control it, for improved response.

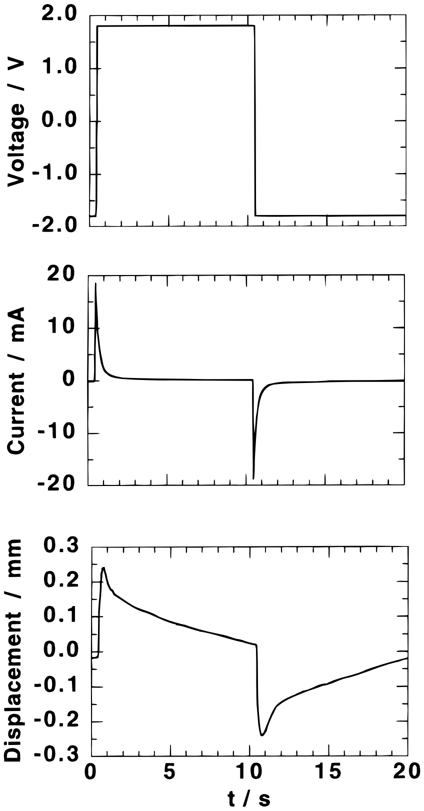

**Figure 8.** Displacement and current response of the water-immersed actuator composed of the Au−Nafion composite (sample no. 2 in Table 1) driven by a 1.8 V rectangular wave.

## Conclusion

In this work, a preparation method for gold−polymer electrolyte membrane composites was established so as to furnish an actuating device capable of large displacement without gas evolution. The essential characteristic for the actuating composite is that gold layers with large conductivity must be formed just on the membrane surface. Suitable composites for these electric stimuli-responsive devices were obtained by the impregnation−reduction method using $[Au(phen)Cl_2]^+$ with Na-asc or $Na_2SO_3$; or $[Au(en)_2]^{3+}$ with Na-asc, as gold precursor and reducing agents, respectively. Polymer actuators based on these composites show large displacement in response to a 2.0 V rectangular wave without visible gas evolution. These actuating devices are now being developed in various fields. Micro devices for medical use, such as an active catheter for intravascular neurosurgery, are considered most promising for practical use. The optimization of the actuator's motion for each application is now being tried by exchanging cations in the membrane or changing electric signals. Further advances in performance and the application are described elsewhere.[36]

**Acknowledgment.** The authors thank Dr. James G. Highfield for helpful discussions.

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