An Electrochemical Actuator Fabricated by Transfer-printing of a Carbon Electrode onto a Cupric-ion-containing Poly(acrylic acid) Gel Surface

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ABSTRACT

Highly functional polymer-gel materials that include highly conductive gels, moving gels, and stimulation-responsive gels are important in a number of applications, including actuators, microrobots, and artificial muscle; hence, the development of new gels with superior properties is an important objective. Herein, we report the fabrication of a flexible electrochemical actuator by the direct transfer of a carbon electrode, formed by screen-printing on a silicone sheet, onto the surface of a poly(acrylic acid) gel containing cupric ions, which was prepared by immersing the poly(acrylic acid) gel in a 0.1M copper sulfate solution. Due to the oxidation of copper and the reduction of cupric ions, when potentials of 0.6V and ~0.7V are alternately applied to the poly(acrylic acid)-cupric-ion gel actuator, it repeatedly expands and contracts along with concomitant copper-ion redox transformations when immersed in 0.1M aqueous sodium perchlorate. This actuator demonstrated a 0.29% change in expansion ratio, which is 2.3-times larger than that of a previously reported electrochemical actuator (0.13%) formed with a sputtered gold electrode on a conventional polymer substrate.

Keywords : Poly(acrylic acid), Screen-printing, Electrochemical Actuator

1. Introduction

In recent years, highly functional polymer-gel materials, such as highly conductive gels,12 moving gels,1 and gels that respond to stimulation,4 have attracted attention. Research on such highly functional gels was stimulated by the discovery of gel volume phase-transition phenomena by Tanaka et al.5 The volume phase-transition phenomenon causes a discontinuous volume change in response to an external environmental change, such as temperature,6 light,7 pH,8 electric field,9–12 or magnetic field,13 and volume phase-transition occurs in response to various stimuli, such as ionic strength14 and solvent composition.15 These functions have been applied to actuators, chemomechanical systems such as microrobots, and motor functions that have led to artificial muscle.16

Electrochemical actuators, which are driven by redox reactions in gels, have also attracted attention for applications as nanoscale and micro-scale actuators, micromanipulators, and artificial muscle.17–20 In such a system, an electrode is bonded to a polymer that swells and deswells in response to redox reactions, resulting in changes in gel length. However, the length of the electrode is unchanged; consequently, a force is applied to the electrode, resulting in its bending.21

A poly(acrylic acid) gel can capture multivalent cations, such as cupric ions (Cu++) when cupric ions are injected into the gel, the carboxylate functional groups (COO-) in the polymer chains of the gel become connected through electrostatic interactions involving the cupric ions,2 resultibg in shrinkage and the release of water. On the other hand, Cu is deposited when a negative potential is applied through an electrode, which results in a decrease in the cation concentration and gel swelling through water absorption.

A poly(acrylic acid) gel can accommodate large volume changes when the swelling and deswelling states of the polymer gel are controlled through redox reactions at the redox potential of the cupric ion; therefore, a poly(acrylic acid) gel can be used in an electrochemical actuator. Such an actuator is conventionally formed on a gold-sputtered electrode fabricated on a polyimide substrate;22 however, the hardness of the polyimide substrate is problematic. In particular, the movement and expansion ratio of the gel actuator is limited by the stiffness of the polyimide substrate.26 In order to solve this problem, in this study we fabricated a novel electrochemical actuator in which a carbon electrode is formed directly on a cupric-ion-containing poly(acrylic acid) gel by the transfer-printing technique, as shown in Fig. 1(a) and discussed in detail below.

An actuator consisting of poly(acrylic acid) with printed cupric ions has been reported.28 It can design the distribution of cupric ion on the gel, but requires a copper electrode to print cupric ion. Therefore, it is rather difficult to prepare fine and complicated patterns especially for large area at low cost. On the other hand, our method does not require the copper electrode in the same pattern desired, and is facile in large-lot production.

2. Experimental

2.1 Preparing the poly(acrylic acid) gel

The poly(acrylic acid) gel was prepared by radical polymerization using acrylic acid as the monomer, N,N'-methylenebisacrylamide as the crosslinking agent, tetramethylethylenediamine as the polymerization accelerator, and ammonium persulfate as the polymerization initiator, according to a previous report.26 The polymerization inhibitor (hydroquinone monomethyl ether) was separated from the acrylic acid by distillation under reduced pressure.
2.2 Preparing and evaluating the carbon ink

The carbon-nanofiber carbon ink was prepared as follows. Carbon nanofibers (length: 2–5 mm; diameter: 8–10 µm, Sigma-Aldrich) were mixed with carbon ink (Jojo Chemical, JELCON CH-8) to a loading of 1.5 wt%.

2.3 Fabricating the electrochemical actuator with the cupric-ion-incorporated poly(acrylic acid) gel by the transfer printing of a carbon film

The prepared poly(acrylic acid) gel was first immersed in an aqueous 10 mM CuSO4 solution. The resultant gel is referred to as the “poly(acrylic acid)-cupric-ion gel”. The carbon ink was first screen-printed on a silicone rubber sheet and then dried at 120°C for 30 min. In order to transfer the carbon film onto the gel, the carbon printed on the silicone rubber sheet was attached to the poly(acrylic acid)-cupric-ion gel and then dried at 80°C for 60 min.

2.4 Acquiring polarization curves

All electrochemical experiments in this study were performed using the three-electrode method. Indium tin oxide (ITO) plate (Nippon Sheet Glass, 2 cm × 2 cm, 1.0 mm thick) was used as the working electrode. A platinum wire and saturated KCl/AgCl, respectively. Polarization curves were acquired in 0.1 M sodium perchlorate with a potentiostat (Compactstat, Ivium Corp.) at scanning rate of 1 mV s⁻¹.

2.5 Evaluating the performance of the actuator

To evaluate the performance of the actuator, potentials of +0.6 V and −0.7 V (vs. sat. KCl/Ag/AgCl) were repeatedly applied to the working electrode in 0.1 M sodium perchlorate solution for 5 cycles. The movement of the actuator was recorded using a digital camera (OLYMPUS, SP-820 UZ) and the radius of curvature (R) and expansion ratio (Δl/l₀) were calculated using following equations

\[ R = \frac{\delta}{(\delta^2 + l^2)}, \]

\[ \Delta l/l_0(\%) = \frac{2\delta l}{(\delta^2 + l^2)} \times 100, \]

where \( l_0 \) is the initial length of the gel, \( \Delta l \) is the gel-length displacement, \( d \) is the thickness of the carbon film, \( l \) is the displacement of the gel in the height direction, and \( \delta \) is the displacement of the gel in the horizontal direction.

3. Results and Discussion

3.1 Preparing and evaluating the carbon ink

The carbon-film electrode needs to be highly flexible and highly conductive in an electrochemical actuator that uses a poly(acrylic
3.2 Preparing the actuator by transfer printing

The poly(acrylic acid) gel is highly water-absorbing and is composed of approximately 95% water. On the other hand, since the ink generally contains an organic solvent, it is hydrophobic and does not exhibit good affinity for the poly(acrylic acid) gel; therefore, the ink could not be directly printed onto the poly(acrylic acid) gel with fastness in our preliminary experiment. A high crosslinking density is achieved by incorporating cupric ions into the poly(acrylic acid) gel, which expels water from the gel; consequently, the poly(acrylic acid) gel for the carbon ink is expected to attach strongly. Hence, we first determined the concentration of cupric ions that the poly(acrylic acid) gel can contain by referring to a previous report. The poly(acrylic acid) gel was found to capture a sufficient amount of cupric ions when it was immersed in a 0.1 mM copper sulfate solution. If the concentration of copper sulfate is too high, the gel does not exhibit swelling due to increase in the degree of cross-linking, whereas low concentration leads to insufficient collapse of the gel. Furthermore, the actuator may move slowly if the concentration of copper in the poly(acrylic acid) gel is too high, since a large number of cupric ions needs to be reduced on the carbon-fiber substrate when the substrate is pressed. Figure 3 shows photographic images of a carbon-film electrode formed on the gel: (a) side view, and (b) top view.

Figure 4. (a) Cathodic polarization curve and (b) anodic polarization curve in 0.1 M aqueous sodium perchlorate acquired using a cupric-ion-containing poly(acrylic acid) gel printed with a carbon electrode. The anodic polarization curve was recorded after the cathodic polarization experiment. The scanning speed was 1 mV/s.

3.3 Acquiring polarization curves

We first recorded the cathodic polarization curve for the actuator, which reveals that the current increases gradually and exponentially at potentials lower than 0 V. The cupric-ion reduction current increased from 0 V. A peak current was observed near −0.6 V (Fig. 4(a)). Since sufficient reduction was observed below −0.6 V, the potential of the cupric-ion reduction reaction was set to −0.7 V in actuator-performance experiments. The anodic polarization curve shows increases in current at potentials higher than 0 V (Fig. 4(b)). A peak current was observed at around 0.6 V; hence, we determined that copper is sufficiently oxidized at a potential of 0.6 V, therefore the copper-oxidation potential was set to 0.6 V in actuator-performance experiments.

3.4 Actuator performance

The mobilities of the actuator at an oxidation potential of 0.6 V and a reduction potential of −0.7 V were determined by recording the anodic and cathodic polarization curves. Firstly, the actuator was bent by immersing it for 1 h in a sodium perchlorate solution.
substrate, which is ascribable to the high formability of a previously reported electrochemical actuator (0.13 \% Eq. (2) (Fig. 6). The changes in the expansion ratio of the present actuator returns to its initial state when a potential of 0.6 V is applied (Fig. 5(c), Supporting Information Movie). We conclude that this is due to reduced copper on the electrode that dissolves to form cupric ions when it oxidized that promotes crosslinking in the gel, which results in release of water and the contraction of the gel, giving rise to the absorption of water and the swelling of the gel (Fig. 5(b), Supporting Information Movie). We confirm that the actuator returns to its initial state when a potential of 0.6 V is applied (Fig. 5(c), Supporting Information Movie). We conclude that this is due to reduced copper on the electrode that dissolves to form cupric ions when it oxidized that promotes crosslinking in the gel, which results in release of water and contraction.

Furthermore, the expansion ratio (\(\Delta l/l_0\)) was calculated using Eq. (2) (Fig. 6). The changes in the expansion ratio of the present actuator was determined to be 0.29\%, which is 2.3-times larger than that of a previously reported electrochemical actuator (0.13\%) formed with a sputtered gold electrode on a conventional polymer substrate, which is ascribable to the high flexibility of the carbon electrode fabricated directly on a gel by transfer printing.

4. Conclusion

In this study, we developed a new electrochemical actuator by transfer-printing a carbon electrode on a poly(acrylic acid) gel containing 0.1 mM cupric ions. The actuator was observed to swell and deswell when potentials of 0.6 V and −0.7 V were alternately applied, due to the oxidation of copper and the reduction of cupric ions.

The maximum expansion ratio of the present actuator was 0.29\%, which is 2.3-times larger than that of a previously reported electrochemical actuator. As a result, we confirmed that the driving force of an actuator can be improved by forming a flexible electrode directly on a gel by transfer printing.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.19-00063.

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