Full Length Article

Formation of a gold nanoparticle layer for the electrodes of ionic polymer–metal composites by electroless deposition process

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ABSTRACT

We investigated the reduction conditions of Au-deposited ionic polymer–metal composites (IPMCs) to form gold (Au) electrodes on the surface of a sulfonated tetrafluoroethylene-based fluoropolymer-copolymer (Nafion), as the ionic polymer membrane, through the electroless deposition of nanoparticles (NPs) layer. The size and distribution of Au NPs formed on the surface of the ionic polymer varied depending on the concentration from 0.25 to 1 mM of sodium L-ascorbate aqueous reducing agent solution and reduction duration of up to 6 hrs. The size and distribution of the Au NPs with different reduction conditions were confirmed to be closely related to the thickness and uniformity of the Au IPMC electrodes. Changes in the Au NP layer formed on the surface of the Nafion entailed changes in the electrical resistance and electromechanical behavior of the IPMCs with Au electrodes.

1. Introduction

Ionic polymer–metal composites (IPMCs) are smart materials that exhibit mechanical motility under an applied voltage. Conversely, they produce voltage under a mechanical deformation. Thus, they have been applied as artificial muscles, robotic actuators, and electrical sensors due to their electromechanical properties [1–6]. Typically, IPMCs are composed of an ionic polymer membrane and both sides of the membrane are chemically deposited or physically coated with a conductive material as electrodes. It is believed that conducting materials exhibit a significant role toward determining the electromechanical properties of IPMCs. Therefore, many studies have been performed with regard to applying various conducting materials as IPMC electrodes [7–11]. In general, IPMC electrodes must possess outstanding corrosion resistance and mechanical durability with high conductivity because they usually move repeatedly under aqueous environments. Therefore, noble metals, which are chemically very stable, are primarily used as IPMC electrodes. Among these noble metals, gold (Au) possesses an excellent electrical conductivity that is approximately 4 times greater than platinum. Additionally, Au possesses a high overvoltage for the evolution of hydrogen and oxygen in aqueous solutions. Furthermore, Au is more flexible and resistant to cracks related to repetitive loading and mechanical stress [12–17].

Various methods with regard to forming Au layers on the surface of ionic polymers have been reported. Among those, the electroless deposition of nanoparticles (NPs) has been widely applied to many applications. It uses various Au precursors and reducing agents to reduce Au ions in an aqueous solution. In this process, Au NPs form on the surface of ionic polymers through precipitation. Therefore, they can be deposited on the surface of ionic polymers through control over the reduction conditions. This method can be used to efficiently develop a uniform and robust Au layer with less effort than other methods.

However, although several studies have reported on the electroless deposition of Au NPs, few studies have been performed using the reduction conditions of Au-deposited IPMCs, the most important variable for the formation of Au NP layers. Therefore, this study investigated changes in resistance and electromechanical properties according to the reduction conditions of Au NPs in the electroless deposition from a microstructural perspective.

2. Experimental procedures

2.1. Materials and preparation of the Au complex

A sulfonated tetrafluoroethylene-based fluoropolymer-copolymer (Nafion) with a thickness of 183 μm was used for the ionic polymer

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membrane. Gold (III) chloride hydrate (HAuCl$_4$·xH$_2$O), 1,10-Phenanthroline (C$_{12}$H$_8$N$_2$), and ethyl alcohol were used for the preparation of dichlorophenanthroline gold (III) chloride ([Au(phen)Cl$_2$]Cl), a gold precursor. Sodium L-ascorbate (Na-asc, C$_6$H$_7$NaO$_6$) was used as a reducing agent. Lithium chloride (LiCl) was used to increase the conductivity of membrane and deionized water was used to clean the membranes and prepare the IPMCs. All the reagents used in this study were purchased from Sigma-Aldrich, US.

The Au precursor, [Au(phen)Cl$_2$]Cl was prepared according to the experimental procedures reported in Ref. [12]. C$_{12}$H$_8$N$_2$ (1 g) in ethyl alcohol (10 ml) was added to a stirred solution of HAuCl$_4$·xH$_2$O (1 g) in ethyl alcohol (10 ml). The solution mixture with a yellow precipitate was heated at 50 °C until turning completely orange. The prepared solution was vacuum-filtered with a polyethersulfone filter (200 μm pore size). The synthesized Au complex was washed several times with ethyl alcohol and dried in an oven at 60 °C for 24 hrs.

2.2. Cation exchange and the reduction process

The Nafion was impregnated with an aqueous solution of 5 mM [Au(phen)Cl$_2$]Cl at room temperature for 24 hrs. The impregnated Nafion was reduced using a Na-asc aqueous solution (varied content from 0.25 to 1 mM) at 70 °C for up to 6 hrs.

2.3. Characterizations

Surface morphology and cross-sectional imaging of the Au-deposited Nafion was observed with a scanning electron microscope (SEM, TM3030, Hitachi) and a field emission scanning electron microscope (FE-SEM, JSM 6700F, Jeol). Qualitative analysis of the Au NP layer was performed using an energy dispersive spectrometer (EDS, Mini-SVE 2107, Bruker). The electric resistance was determined using a probe station (Unitek). Electromechanical responses of the prepared samples were measured using a laser displacement sensor (optoNCDT-1401, Micro-Epsilon) with a 0.5 × 2.0 cm sample size in a test setup composed of a signal generator (FG-7002C, EZ digital), power amplifier (LVC-608, AE Techron), and a DAQ (SCB-68, National Instruments). The prepared samples were clamped in a cantilever configuration in water with a free-length of 1.9 cm. The displacement was monitored 1.7 cm away from the clamp contacts. Voltage, current, and displacement responses were recorded using a data acquisition system (LabView 8, National Instruments) under alternating current (AC).

3. Results and discussion

Fig. 1 shows photographs of the Nafion under different conditions. As can be seen in Fig. 1a, the original Nafion was transparent and colorless but turned yellow after impregnation with the [Au(phen)Cl$_2$]Cl aqueous solution (Fig. 1b). In the photographs of the Au-deposited Nafion using different concentrations of the reducing agent for 5 hrs, samples reduced with 0.25 mM of Na-asc aqueous solution (Fig. 1c) exhibited the typical color of Au and gloss; however, the color of the samples became darker and less glossy as the concentration of the

reducing agent increased. Additionally, the electric resistance of the sample increased. The sample reduced with 0.25 mM exhibited an electrical resistance of less than 1 Ω, which was uniformly measured throughout the specimen. However, the electrical resistance of the reduced samples (0.5 and 1 mM) was around 10 and 20 Ω, respectively. Therefore, sample microstructural analysis was performed to determine the cause of these changes.

Fig. 2 shows surface morphologies of the Au-deposited Nafion under different reducing agent concentrations. Several Au NPs were found on the surface of the sample reduced with 0.25 mM of the Na-asc aqueous solution (Fig. 2a). In this sample, a relatively dense surface was formed compared to the other samples as the reduction proceeded, filling up empty space due to continuous heterogeneous nucleation and grain growth. However, in the case of the samples reduced with 0.5 and 1 mM of the Na-asc aqueous solution (Fig. 2b and c, respectively), NPs were not found because the reducing agent with a higher concentration yielded a relatively rapid reduction of Au ions and the reduction process was terminated earlier. Additionally, the deposited Au NP layers were not dense compared to the sample reduced with 0.25 mM of the Na-asc aqueous solution and cavities that were micrometers deep were also observed. The presence of large cavities prevented the transfer of electrons, thereby increasing the electrical resistance of the sample.

Surface morphologies of the Au-deposited Nafion reduced with the 0.25 mM Na-asc aqueous solution for up to 6 hrs can be seen in Fig. 3. During the initial stage of the reduction, the Nafion surface acted as heterogeneous nucleation sites for the deposition of Au NPs in aqueous Au ion solutions. Therefore, Au NPs were distributed on the surface of the Nafion as can be seen in Fig. 3a. A small number of agglomerated Au NPs of approximately 1 μm in size were partially observed because the surfaces of the Au NPs that were reduced earlier acted as additional heterogeneous nucleation sites. With an increased reduction time, the surface of Nafion was observed to be further covered with continuous heterogeneous nucleation and growth of Au NPs. For samples that were reduced for 4 hrs, the Nafion surface was observed to be covered with Au NPs. Samples that were reduced for more than 4 hrs were also covered with Au NPs on all surfaces.

Fig. 4 shows the cross-sectional morphology and component analysis of the prepared Au-deposited Nafion. In the sample that was reduced for 1 hr (Fig. 4a), a discontinuous Au NP layer with hundreds of nanometers thick was formed on the surface of the Nafion. In the sample that was reduced for 2 hrs (Fig. 4b), the thickness of the Au NP layer increased and formed continuously compared to the sample that was reduced for 1 hr. However, the Au NP layer featured small cavities and a reduced density. In terms of electrical properties, these cavities would act as defect that prevents the transfer of electrons. Therefore, they contributed toward increasing the electric resistance within the Au NP layer. A relatively dense Au NP layer with a thickness of approximately 2 μm was formed in the sample that was reduced for 4 and 6 hrs (Fig. 4c and d). The increased thickness of the Au NP layers was due to the continuous nucleation and growth of Au NPs on the surface of the Au particles that formed earlier, as can be seen in the surface morphologies of Fig. 3. There was not a large variation in relative thickness with reduction periods longer than 4 hrs. Fig. 4e presents the
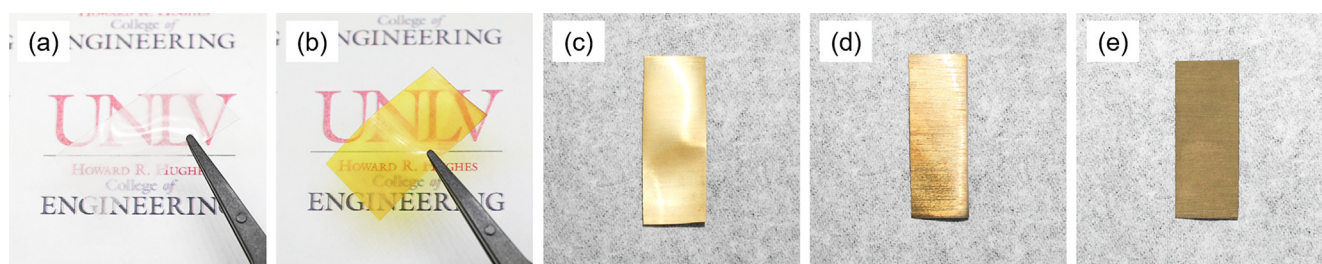

Fig. 1. Photographs of the Nafion under different conditions: (a) prior to impregnation, (b) after impregnation. Au-deposited Nafion reduced with a (c) 0.25, (d) 0.5, and (e) 1.0 mM Na-asc aqueous solution for 5 hrs.
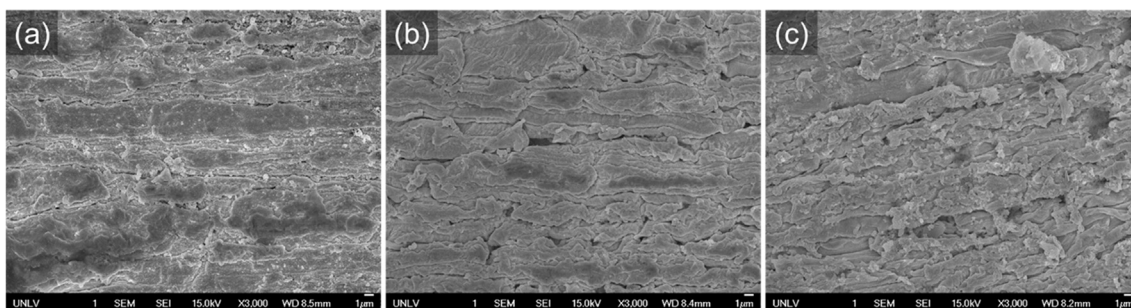
Fig. 2. Surface morphologies of Au-deposited Nafion under different reducing agent concentrations: (a) 0.25, (b) 0.5, and (c) 1 mM.
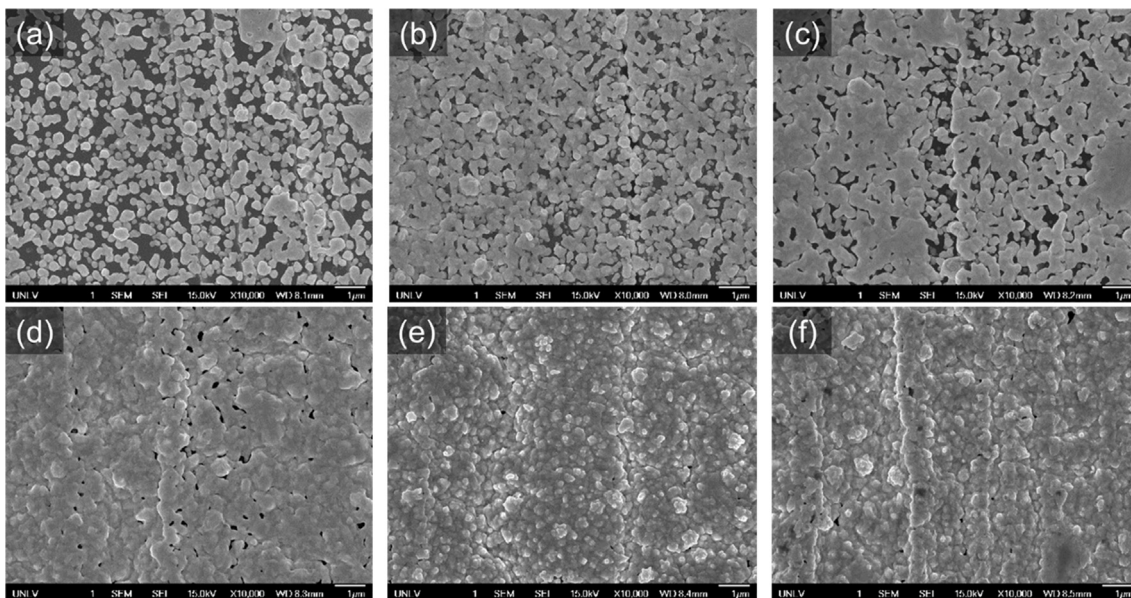

Fig. 3. Surface morphologies of the Au-deposited Nafion reduced with a 0.25 mM Na-asc aqueous solution for (a) 10 min, (b) 30 min, (c) 60 min, (d) 120 min, (e) 240 min, and (f) 360 min.
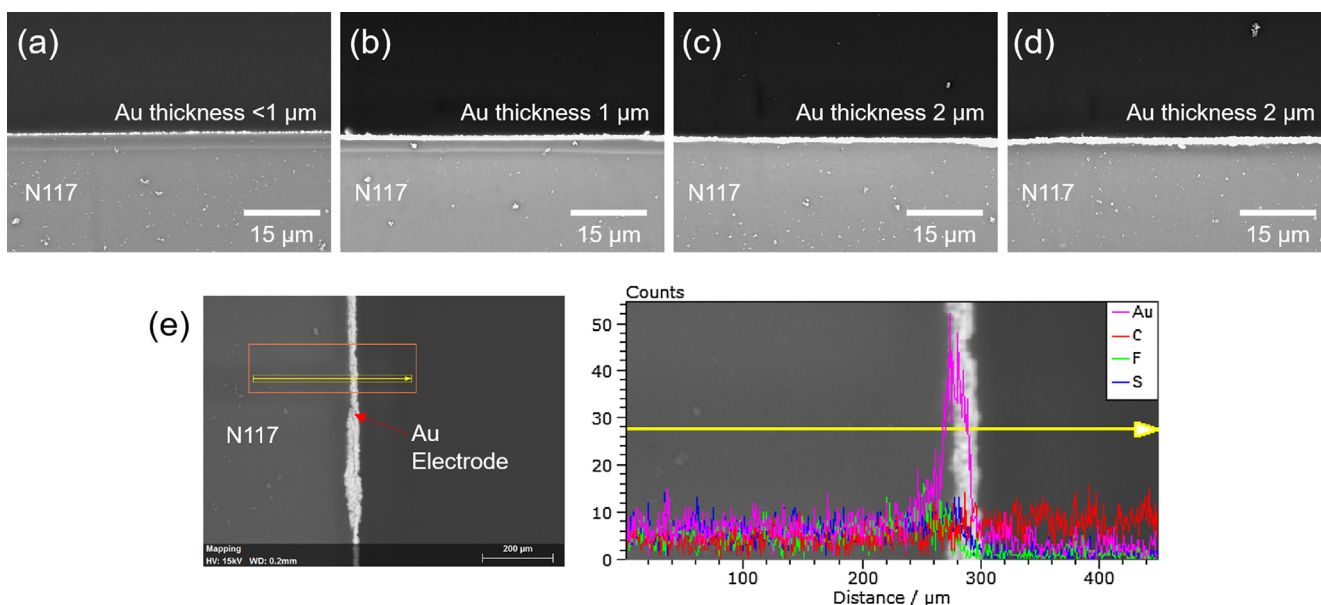

Fig. 4. Cross-sectional images of Au-deposited Nafion reduced with a 0.25 mM Na-asc aqueous solution for (a) 1, (b) 2, (c) 4, (d) 6 hrs, and (e) EDS analysis results of the Au-deposited Nafion.
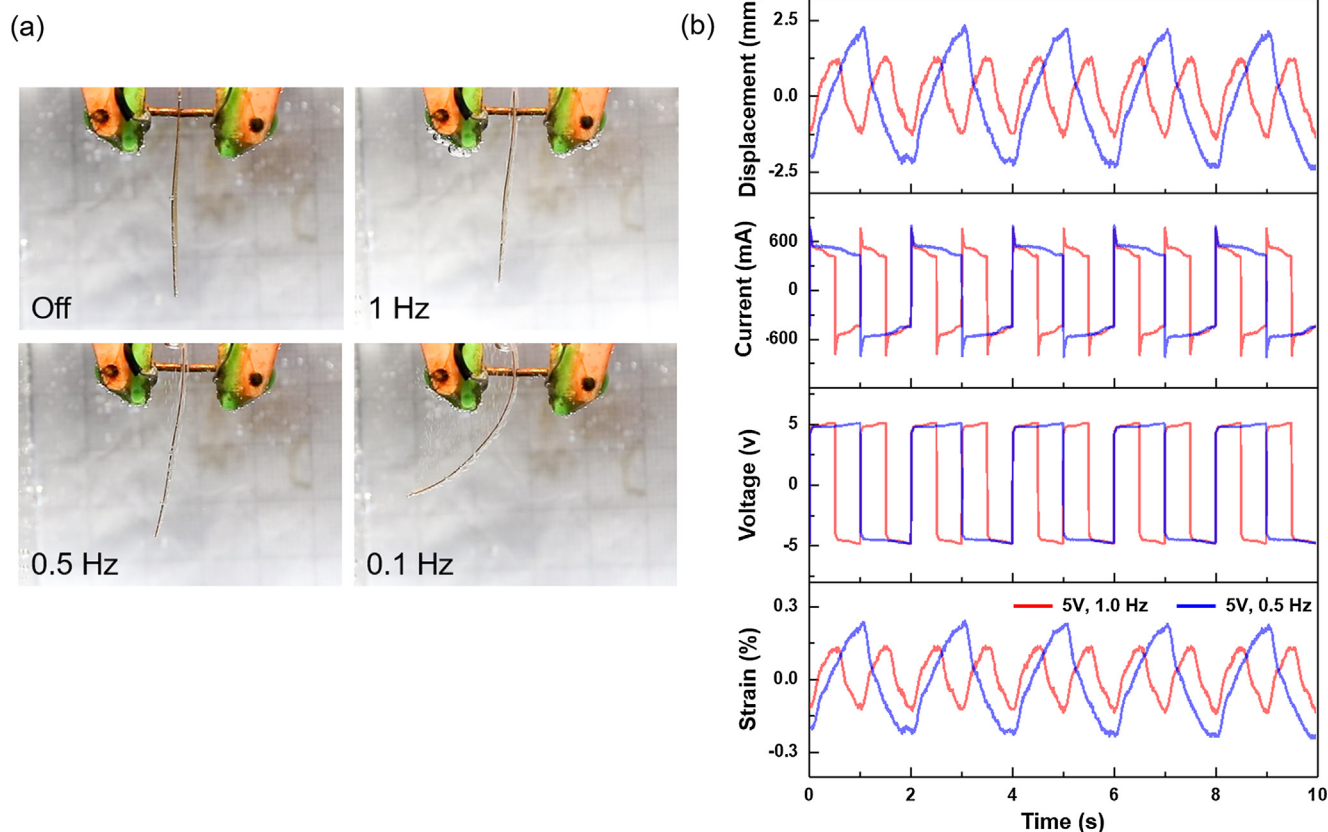
(a)

(b)

Fig. 5. (a) Photographs and (b) corresponding displacement, current response, voltage, and bending strain of Au-deposited Nafion reduced with a 0.25 mM Na-asc aqueous solution for 4 hrs driven by 5 V square-wave at a frequency of 0.5 and 1.0 Hz.

EDS analysis of the cross-sectional images (line scan), which elucidated that the Au layer formed on the surface of the Nafion.

Photographic images of Au-deposited Nafion at maximum displacement with/without an applied voltage (± 5 V, AC) under varying frequencies (0.1, 0.5, and 1.0 Hz) can be seen in Fig. 5a. As the frequency decreased to 0.1 Hz, a notable displacement response was observed in the sample. Fig. 5b shows the measured voltage, current, corresponding displacement response, and bending strain for the Au-deposited Nafion as a function of time at ± 5 V ac square-wave input at frequencies of 0.5 and 1.0 Hz. The measured tip displacement (δ) was converted to the bending strain (ε) according to the following relation: $\varepsilon \cong \frac{\delta t}{L^2 + \delta^2}$, where L is the free length and t is the thickness of the IPMC. As can be seen, the displacement response of the specimens at higher frequencies (1.53 mm, 1.0 Hz) were shown to be lower than the response (2.24 mm) at 0.5 Hz due to the limited charging time at higher frequencies [18].

4. Conclusion

In this study, an Au NP layer was deposited on the surface of Nafion by the reduction of [Au(phen)Cl$_2$]Cl using different concentrations of a Na-asc aqueous solution. As the Na-asc concentration increased, the color of the deposited Au NP layer was observed to become darker and less glossy; the surface of the deposited Au NP layer was also uneven and the electrical resistance of the samples increased by at least 20 times (from 1 to 20 Ω, approximately). After reducing for up to 6 hrs using a 0.25 mM Na-asc aqueous solution, Au NPs that reduced on the surface of the Nafion during the initial reduction process were confirmed to gradually form an Au NP layer with a thickness of about 2 μm due to continuous heterogeneous nucleation and growth. Additionally, electromechanical behaviors of Au-deposited Nafion were investigated including the corresponding displacement, current response, measured voltage, and bending strain driven by 5 V rectangular waves at different frequencies.

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