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# The Structure and Performance of Ionic Polymer-Metal Composite Actuators Prepared via Electroless Plating Process Using Various Alcohols

*Jang-Woo Lee, Young-Tai Yoo**

**Summary:** Nafion$^{TM}$-based ionic polymer-metal composite (IPMC) actuators were fabricated using an electroless plating method. This study aims to improve the formation of Pt electrode in IPMCs employing various alcohols as media in the 1st deposition step instead of water. It was found that ethanol formed a thicker and well-dispersed Pt electrode layer, whereas methanol and n-propanol produced thinner Pt electrodes than water. Especially, IPMCs constructed in ethanol demonstrated a bending displacement comparable to conventional IPMCs processed in water without significant back relaxation attributable to a thicker and well-dispersed Pt electrode and its high capacitance. It is also interesting to note that the IPMCs prepared in n-propanol exhibited the fastest actuation response of all.

**Keywords:** actuator; electrode; electroless plating; IPMC; metal-polymer composite

## Introduction

Ionic polymers are widely used as solid electrolytes in the fields of actuators, electrochemical sensors, secondary batteries, fuel cells, and electrochemical reactors due to the capability of ionic conduction with general properties of polymers.[1–3] Ionic polymer-metal composite (IPMC), or membrane electrode assembly (MEA), is composed of a polymeric electrolyte and platinum (Pt) electrodes on both sides of the polymer membrane. The IPMC under an electric field bends to the positive charged side due to the movement of hydrated metal cations to the negative charged side in the matrix.[4,5]

Electroless plating technique for the formation of platinum electrode is based on chemical reduction. It was postulated that this method offers a good adhesion between metal particles and polymer membrane and an even coverage for the preparation of ionic polymer electrolyte-metal assembly.[6,7] There are abundant papers discussing metal plating processes for preparing IPMC or MEA.[6,8–14] Cha et al. investigated the effect of the number of adsorption/reduction cycles on electroless plating process.[6,8] Liu et al. demonstrated a process for plating Nafion$^{TM}$ with gold by electrostatic self-assembly of colloids suspended in polymer solution.[9] Akle et al. reported a process for fabrication of electrodes, which was prepared via a metal powder (ruthenium dioxide) painting technique utilized in building fuel cell electrodes, followed by sandwiching the pre-treated matrix in between two 100 nm-thick conductive gold foils.[10] Noh et al. fabricated a large surface-area composite actuator via a replication method.[11] Shahinpoor et al. devised the introduction of effective dispersing agents during the chemical reduction process, a stretching technique to stretch the base membrane prior to the Pt composition process, and an additional electroplating of Ag or Cu on the surface of Pt electrodes.[12,13] Lee et al. investigated the effect of additional coating

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Department of Materials Chemistry and Engineering, College of Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Korea
Fax: (+82) 2 444 3490
E-mail: ytyoo@konkuk.ac.kr

processes in which an initial layer of Pt constructed via a conventional impregnation/reduction process was subsequently deposited onto the Nafion™ matrix by an ion coater or a dc sputter.[14]

As documented in the relevant literature, the modification of electroless plating processes, the use of other metal sources, and the design of new processes for manufacturing electrodes are the mainstream. An alternative approach to develop IPMC actuators with improved performance has been proposed here. Alcohols such as methanol, ethanol, and n-propanol as reaction media were employed on the 1st deposition step of the electroless plating process of Pt. The specific features of Pt electrodes formed in the presence of various alcohols and the performances and electrochemical properties of the resulting IPMCs are discussed.

## Experimental Part

### Materials

Nafion™ 117 perfluorosulfonic acid membrane (acid capacity: 0.89 meq $\cdot$ g$^{-1}$, thickness 183 μm), used as a solid polymer electrolyte, was purchased from DuPont. $Pt(NH_3)_4Cl_2$ (purity: 98%) as a platinum salt and $NH_4OH$, $NaBH_4$, $H_2NNH_2$, and $H_2NOH \cdot HCl$ as reducing agents were obtained from Aldrich. Methanol (purity: 99.8%), ethanol (purity: 99.9%), and n-propanol (Purity: 99%) purchased from Samchun Chem Co. were used as received.

### Preparation of IPMCs

The fabrication method of IPMC employed in this study is based on the processes reported in the literature.[12] Nafion™ film was firstly roughened by sandpaper on both sides, followed by cleaning in an ultrasonic cleaner. The membrane was subsequently washed with 3 wt.-% aqueous $H_2O_2$ solution, 1.5 M aqueous $H_2SO_4$ solution, and finally with de-ionized water at 80 °C for 1 h. After that, the 1st deposition process (adsorption/reduction process) for the depth growth of Pt was performed as follows. The membrane was immersed in 0.02 M aqueous solution of $Pt(NH_3)_4Cl_2$ to exchange protons for Pt ions at room temperature for at least 3 h. The membrane was rinsed with de-ionized water and cut to four pieces. The pieces placed in 300 mL of de-ionized water, methanol, ethanol, and n-propanol at 45 °C, respectively and followed by adding 0.5 mL of 30 wt.-% aqueous $NH_4OH$ solution and 3 mL of 2 wt.-% aqueous $NaBH_4$ solution 6 times every 30 min to each bath while stirring. The 1st deposition process was repeated three times. The 2nd deposition process for the additional surface growth of Pt was carried out as follows. The films obtained from the 1st deposition were placed in an aqueous $Pt(NH_3)_4Cl_2$ solution (0.8 g of $Pt(NH_3)_4Cl_2$ in 300 mL of de-ionized water) at 45 °C. Subsequently, 3 mL of 5 wt.-% $H_2NOH \cdot HCl$, 1.5 mL of 20 wt.-% $H_2NNH_2$, and 1 mL of 30 wt.-% $NH_4OH$ aqueous solutions were added 8 times every 30 min. After drying, $Li^+$-form IPMCs were obtained by immersing in 1 M aqueous solution of LiOH at room temperature for 24 h.

### Characterization

A SEM instrument (JEOL, JSM-6380) was utilized for investigating the morphology of Pt electrode layers. Electrical properties of the prepared IPMCs were measured by an impedance analyzer (Zahner, IM6ex) and a digital multi-meter (Agilent, 34411A).

### Actuation Test

An IPMC was cut to the strip of 0.5 cm × 2.5 cm size. For the evaluation of bending performance the strip was supported vertically in air and fixed to 0.5 cm length on both sides, thus the actual effective length of the sample was 2 cm. The electric power was applied by an ac source/analyzer (Agilent, 6811B). The tip force, which is the blocking force at zero displacement, was measured by using a load cell (Dacell, CB1-G150) and tip displacement was measured employing a custom-made Pt clip and a CCD camera as reported in previous papers.[15–17] The tip displacement was considered as the displacement along the horizontal axis only. The deformation response was tested under 3 V dc.

## Results and Discussion

In a typical electroless plating process, water is used as a reaction medium for the expansion of ionic channels of Nafion$^{TM}$ and the dissociation of ion pairs of $SO_3^-$ anion and metal cation.[1–3,18] As shown in Equation (1) and (2), hydroxide anions ($OH^-$) essential to the reduction of Pt cation hardly penetrate the negatively-charged Nafion$^{TM}$ matrix and consequently produce a thin Pt layer.[11] This work is based on the assumption that the higher swelling ratios of Nafion$^{TM}$ in methanol, ethanol, and n-propanol (>50 wt.-%) than that in water (approximately 20 wt.-%) may allow facile diffusion of hydroxyl anions into the Nafion$^{TM}$ matrix. The effect of the alcohols was examined on the 1st deposition step where major Pt electrode layers are formed.

$$[Pt(NH_3)_4]^{2+} + 2e \rightarrow Pt + 4NH_3 \qquad (1)$$

$$NaBH_4 + 8OH^- \rightarrow BO_2^- + Na^+ + 6H_2O + 8e \qquad (2)$$

Since the reducing agents for the electroless plating process are available in aqueous form, the total amount of water in the reactor containing an alcohol as a medium for the 1st deposition step increases as the aqueous reducing agents are added to the reactor every 30 min. Therefore the swelling ratio of Nafion$^{TM}$ membrane in the aqueous solution of alcohols for the deposition step is expected to vary depending on the composition, which means that the concentration of the aqueous reducing agents with time affects the formation of Pt electrode layers (see Figure 1). Additionally, it is interesting to note that the water/alcohol ratio at the maximum swelling of the membrane increases with the carbon number of alcohol.

The type of the alcohols on the 1st deposition step affected the formation of Pt electrodes. As shown in Figure 2, the reduction of Pt cations carried out in ethanol produced a thicker and well-dispersed electrode layer compared to in water. This may be attributed to the distance between polymer chains extended by ethanol, resulting in facile diffusion of hydroxyl anions into the Nafion$^{TM}$ matrix. In opposition to what is expected, methanol and n-propanol formed thinner electrode layers than water did.

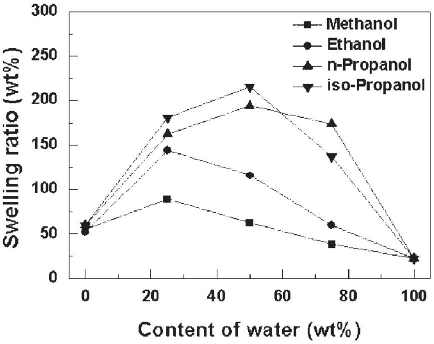

***Figure 1.***
Swelling ratio (wt.-%) of Nafion$^{TM}$ membrane in the aqueous solution of alcohols as a function of water content at equilibrium state and ambient conditions.

Figure 3 shows the surface resistance and the impedance between two electrodes of the pre-IPMCs after only the 1st deposition step with alcohols. The surface resistance of water-based pre-IPMCs was lower than that of alcohol-based ones, whereas the impedance of water-based ones between two electrodes was the highest. These results reflect the possibility of small invisible Pt particles penetrated more deeply in Nafion$^{TM}$ matrix, caused by a deeper penetration of $OH^-$ ions in the matrix soaked in alcohol, although methanol and n-propanol formed thinner Pt layers than water from the SEM images.

In Figure 4, methanol-based IPMCs showed the response of displacement was slow and its tip force was very weak. In the case of n-propanol-based IPMCs, the bending response and the back relaxation after full bending were the fastest among all samples. Ethanol-based IPMCs showed a

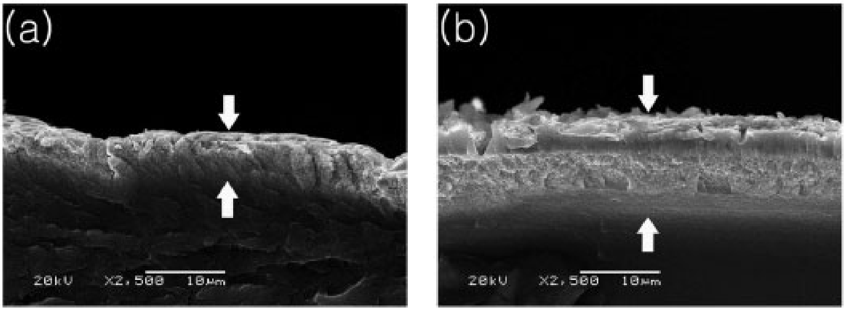

***Figure 2.***
SEM micrographs of cross-section of IPMCs fabricated in the presence of various alcohols as reaction media on the 1st deposition step: (a) water and (b) ethanol.

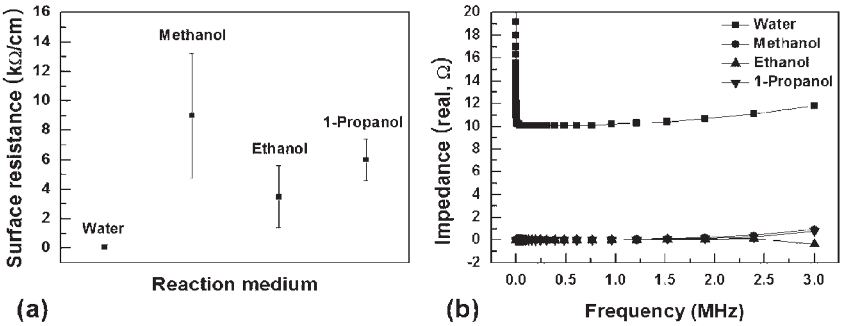

***Figure 3.***
Surface resistance (a) and impedance between two electrodes (b) of pre-IPMCs after only the 1st deposition step.

fast bending response with very limited back relaxation behavior in contrary to an expectation that the back relaxation may increase with the bending actuation speed. The interesting actuation behavior of the ethanol-based IPMCs may be related to the large charge accumulation in the large interfacial area between Nafion™ matrix and the Pt electrode layer due to its thick, dense, and well-dispersed Pt particle

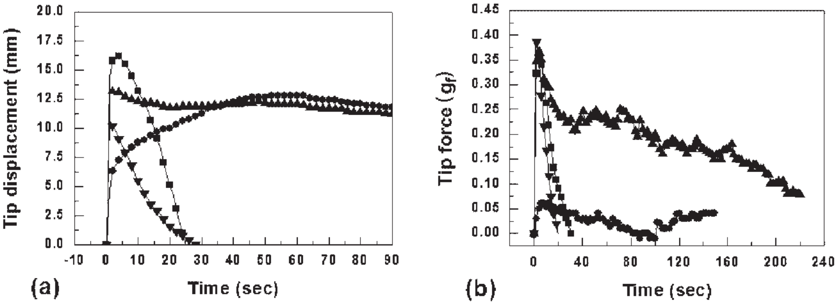

***Figure 4.***
Bending behavior vs. time of $Li^+$-form IPMCs (0.5 × 2.5 cm) fabricated in the presence of various alcohols (a) tip displacement and (b) tip force: (■) water, (•) methanol, (▲) ethanol, (▼) n-propanol. The deformation responses were measured under 3 V dc.

morphology, whereas the fastest actuation behavior of the n-propanol-based IPMCs may be attributed to the small charge accumulation resulting from the rapid charge flow through small Pt particles properly distributed across the membrane.

## Conclusions

The electroless plating process carried out in various alcohols formed a different morphology in the Pt electrode layer of IPMC. Especially, ethanol-based IPMCs exhibited a thick and well-dispersed Pt electrode layer, displaying a fast bending response without significant relaxation behavior, while n-propanol-based IPMCs showed the fastest actuation behavior under an electric potential probably due to a deeper distribution of small Pt particles. Consequently, the thickness and morphology of the electrode layer in IPMCs could result in different actuation behavior of IPMCs. Thus, the actuation performance of IPMCs can be controlled by changing media in the electroless process.

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