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Humidity sensor based on the ionic polymer metal composite

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ABSTRACT

In this paper, a novel method for fabrication of an ionic polymer-metal composite (IPMC)-based humidity sensor is developed and optimized. IPMC is a kind of smart material that can work as a sensor or an actuator in wet environments or liquids. Poor adhesion between electrodes and the polymer and peeling off phenomenon are common problems in IPMC fabrication. Mechanical roughening, plasma treatment of the polymer surface and sputtering a thin layer of Ti and Cr as adhesion layers between polymer and Au electrodes are proposed to solve these issues. Different fabricated IPMC electrodes were then used as a capacitor to measure the relative humidity variations at different deflections and relative humidity conditions and the results have been compared. Our results show that IPMC using Au with 990 nm thicknesses worked properly and a sensitivity value of 13.43% was achieved.

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1. Introduction

Ionic Polymer Metal Composites (IPMCs) are kinds of Electrically Activated Polymers (EAP) that have attracted so much attention as a sensor or actuator in different fields of science and technology [1–5]. Recent applications of IPMC sensing capability is formed to measure the displacement, pressure, humidity, force and structural health monitoring [6–13]. The biological compatibility of the IPMC sensors is favorable [14] and they are scalable to be realized with micro fabrication which is suited for in vitro applications [15,16]. This sensor generally consists of an electrically activated polymer layer (usually Nafion®) sandwiched by two metal electrodes. Inside the polymer, anions, which are covalently bound to the polymer chains, are balanced by mobile cations. It is able to bend sharply through electrical conduction and has two major advantages of high curvature and high sensitivity. IPMCs have innate sensing properties in which a force or deformation on an IPMC beam produces a measurable electrical parameter (usually capacitance or resistivity). Another amazing feature of this material is that different electrical responses are seen at different humidities, which is a key for developing a sensitive humidity sensor.

There is a major problem during the fabrication of an IPMC. The adhesion between the polymer and the electrode is a challenging part of fabrication. To solve this problem previously, electroless plating method had been used to fabricate the electrode layers, but this time-consuming process needed some expensive metal salts such as [Pt(NH3)5]Cl2 and resulted layers with about 20 μm thickness [2,17–18].

In this work, we have developed a new method of simple physical approaches with low cost and short processing time for fabricating IPMC multi-sensor. Our approach includes surface roughening by sand paper and oxygen plasma and then using a thin layer of sputtered Ti or Cr as an adhesion layer before Au electrode deposition. Then, we have compared the effect of different thicknesses of Au as the electrode and used the fabricated devices in humidity-capacitance measurements. The effect of the deflection on the capacitance during humidity measurement was also studied.

The interesting feature in this study is showing the fact that the manufactured IPMC which normally is used for force sensing, can be used at the same time as a humidity sensor or an actuator. Developing a sensor which can measure different characteristics at the same time by itself can be a huge step; e.g. by measuring the induced voltage on the electrodes, one can sense the amount of mechanical force and deflection of the membrane. At the same time, analyzing the capacitor, induced between two electrodes, results in the relative humidity. In this article, the possibility of using this system as a humidity sensor and an actuator at the same time has also investigated. To do so, we have analyzed the IPMC performance at different deflection to calibrate the deflection induced changes in the capacitance. This means that even when the system
Fig. 1. The SEM micro-graph of a Nafion surface without roughening (left) and roughened Nafion surface (right).

Fig. 2. Optical microscope pictures of: Cr/Au electrodes, (a) without roughening and plasma, (b) just with roughening, (c) with roughening and plasma, Ti/Au electrodes, (d) without roughening and plasma, (e) just with roughening, (f) with roughening and plasma, (g) peel-off of Ti/Au electrode.

Table 1
Sheet resistance of different samples before and after 72 h soaking in NaOH.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Specimen</th>
<th>Before immersion (Ω/sq)</th>
<th>After immersion (Ω/sq)</th>
<th>Absolute change (Ω/sq)</th>
<th>Relative change</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti/Au (350 nm)</td>
<td>0.602</td>
<td>0.632</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>Ti/Au (990 nm)</td>
<td>0.548</td>
<td>0.581</td>
<td>0.033</td>
<td>0.06</td>
</tr>
<tr>
<td>3</td>
<td>Cr/Au (350 nm)</td>
<td>2.32</td>
<td>2.58</td>
<td>0.26</td>
<td>0.11</td>
</tr>
</tbody>
</table>

is bent, because of a mechanical force from an external source (or an applied voltage), the effect of this deflection on the capacitance has been clearly investigated, and thus, the exact relative humidity value can be extracted.

2. Experimental details

2.1. Sand papering pre-treatment

The first step of IPMC manufacturing is pre-treatment of Nafion (Dupont Nafion® 117) sheets. Despite the common fabrication
methods, using chemical methods and metal reduction, we have applied physical deposition methods. One of the challenging problems in fabricating IPMC is peel-off phenomenon of the deposited metal electrodes, which is caused by a 10% expansion in IPMC volume after immersing in water, and low surface energy in ionic polymer [6]. Because of physical nature of metal deposition using RF sputtering method, there were no satisfying adhesion between electrodes and polymer. Poor adhesion shows itself in electrodes peeling off or metal cracks which sometimes can be seen on the whole surface of electrodes. Electrodes peeling off and the created cracks cause an increase in resistance, and finally an open circuit in the metal contact, and smashing the electric field. To overwhelm this issue, a following new method is developed:

1. After an accurate cutting process to $13 \times 5$ mm$^2$ pieces by Nd-YAG laser cutting machine, the nafion sheet of the deposited metal electrodes was roughened by sandblasting or sandpapering (using dry sandpaper grit 5000) and micro scale features was formed on its surface.
2. To clean oil and organic pollution which was created through former processes, the samples were ultra-sonicated for 1 h in acetone.
3. By boiling at 90 °C 2M HCl (Merck) for 30 min, H$^+$ ions were penetrated into the polymer matrix and at the same time most of the metallic and residual organic contaminations were removed from the membrane.
4. To extract the residual acid from the membrane, it was boiled in DI water for 30 min.

2.2. Surface activating processes

As mentioned before, by surface roughening a plenty of micro size features were formed on the polymer surface. Fig. 1 shows SEM top-view micrographs of two prepared sheets with and without roughening step. Argon plasma can be used to improve hydrophilic properties of the polymer surface and simultaneously create some extra surface roughness. However, as reported previously, it reduces the proton conduction that will in turn reduce the adhesion between the electrode and the polymer [19], thus, oxygen plasma was used instead. Oxygen plasma not only increases the hydrophilic characteristics of the surface but also creates some nano-features due to oxidation process of the polymer. On the other hand, roughening will enhance the mechanical adhesion by anchoring the metal particles. Oxygen plasma was used with 50 sccm flow rate, 250 W power, for 60 s.

2.3. Cr/Au electrodes deposition

Combination of Cr and Au was investigated as one of the candidates for the electrode deposition [20]. Cr was used for its high surface energy and in turn high adhesion in micro fabrication processes. After the surface roughening and activating processes, Cr was deposited on the specimens by electron beam evaporation. Deposition was done with 1 A/sec rate at $2 \times 10^{-3}$ Torr pressure. By this method, two set of samples were prepared, one with 150 nm and another with 5000 nm thick Cr layer. Each set had 3 types of samples: The first type didn’t have any physical roughening and surface activation. The second type included a sample which had just a surface roughening process and without surface activation, and the final sample was processed with both surface roughening and surface activation process. To improve the adhesion force between polymer and electrodes, the temperature of the substrate was raised to 150 °C during deposition.

To have improved electrode surface resistance and prevent any metal oxidation, a 350 nm layer of Au was deposited on the Cr layer in the same deposition but at 140 °C temperature.

By mechanical roughening process through the sand papering and sand blasting, some micro- and nano- features were formed on the surface of polymer, these uneven features on the polymer surface can play an important role e.g. in IPMC biosensing applications and are capable of adsorbing higher number of the sensing element compared to a smooth surface. The roughening process thus increased the final surface area which can positively affect the sensing characteristics. Also they can act as micro- and nano-anchor for metal particles and resulted in more stable adhesion between polymer and metal layer.

Fig. 2 shows three different specimens with Cr/Au deposition. As it shows in the figures, there were very wide cracks and also up and downs on its electrode in a sample with neither roughening nor plasma exposing (Fig. 2a). On the other hand, cracks on the roughened specimens were very thinner and smoother (Fig. 2b).

Also as the thickness of Cr layer increases, the width of the cracks was increased. Because increasing the thickness of Cr layer accompanied by increasing in the process time and so increasing in the temperature of the metal and polymer. Inordinate increase in temperature leads to huge expansion and contraction of polymer and metal layers which resulted in wider cracks. It can be seen that due to difference in the expansion coefficient of the metal and the polymer, after Au deposition cracks were still remained on the electrodes. So the sample with 500 nm Cr and 350 nm Au wasn’t useful.

The quick visual comparison between these samples showed that the mechanical roughening and plasma exposing have decreased the number and width of cracks remarkably. There was no peel-off observed in the samples (see peel-off phenomenon in Fig. 2g) which were pretreated by sand paper and exposed to oxygen plasma which means mechanical roughening has much higher...
impressive effects on the adhesion between polymer and metals compared to other treatments.

2.4. Ti/Au electrode deposition

Another plausible choice for electrode deposition which was evaluated in this study was Ti/Au. Because of the nature of sputtering method, the temperature of process won’t rise up more than 80 °C during the whole process, so the expansion and contraction phenomena didn’t affect the metal layers. In this approach, a thin layer of Ti serves as the adhesion layer and Au plays the role of the electrodes. By using a thin layer of Ti, adhesion force between Au and polymer is improved. Thus, a 150 nm thick Ti layer was primarily sputtered on the Nafion membrane followed by a 350 nm thick Au layer deposition (sample no. 1 in Table 1). As shown in Fig. 2f, the surface of the deposited electrodes is very smooth. To compare the quality of the electrodes, for sample no. 2 in Table 1, Au was deposited to reach 990 nm thick layer. Fig. 3 shows a schematic picture of the IPMC sensor using Ti/Au contacts with an inset showing the magnified cross-section. Next was to replace the cations in the polymers to achieve an improved performance.

It is vital not to break the vacuum between Ti and Au deposition. Ti is normally used as an adhesion layer of the metallization process. Fig. 2f shows Ti/Au electrode on the Nafion after mechanical roughening and plasma exposing. Comparing the specimens fabricated by Ti/Au electrode and Cr/Au showed that the number of cracks on the Ti/Au and their width were much lower. Finally, specimens were soaked in NaOH for 72 h to replace the H+ with Na+. This process is carried out in 1M NaOH solution. After this process, specimens rinsed with DI water.

2.5. Humidity sensor setup

Fig. 4 shows the setup for humidity measurement using the fabricated IPMC. This setup consists of a sealed cubic glass container (20 × 20 × 20 cm³) with an inlet from a bubbler. Humidity of the sealed area was controlled and measured in parallel with a commercial humidity meter (HNG, DT3) which placed in the cubic glass for setup calibration at room temperature (25 °C). Output sig-
nals, taken from a SANWA PC-710 Digital Multi-meter, were shown simultaneously on the laptop monitor during the measurements. An air pump was used to pump in a water bubbler and control the humidity inside the container.

3. Results and discussions

3.1. Sheet resistance measurement

By measuring the surface resistance of the deposited electrodes, we could analyze the quality of the metallic layers and the durability of the fabricated IPMC. High resistance shows presence of lots of cracks on the surface. Surface resistance measurement of electrodes is done by a four point probe method before and after 72 h immersion in NaOH solution. The results are shown in Table 1.

As is illustrated in this table, there is an almost significant increase in the resistance of the Cr/Au sample after immersion process. This was occurred due to the increased number of cracks, generated during the volume expansion process due to the ions' diffusion into the sheet. Despite that, the absolute resistance variation is about an order of magnitude lower in Ti/Au series because of good adhesion at the interface of metal and polymer. In order to show the reliability of the deposited contacts, the normalized resistance of one side of the electrode (Ti/Au (≈1 μm)) has been plotted versus time in Fig. 5. It can be seen that after 7 days the resistance value became saturated and no variation was observed afterwards. Therefore, in order to have stable outputs, all of the measurements were taken after 7 days from fabricating IPMC.

It is worth mentioning here that there is a great difference between thickness of electrodes fabricated by this method (less than 1 μm) and other conventional methods such as electroless plating (10–20 μm reported elsewhere [1,9,18]). But considering the surface resistance and electrode resistance, this method not only can promote the scaling down potential, but also achieved surface resistance and sheet resistance much lower than other methods. By decreasing the thickness of IPMC, the flexibility and compliance of the sensor/actuator will increase which creates a great potential for MEMS and bio applications.

3.2. Humidity measurements

In order to obtain the exact value of the capacitance without any effect from the previous measurement, after each capacitance measurement, the sensor was left outside the container for 10 min. This could give us the exact C value compared to the room condition. Fig. 6 displays the capacitance response of the sensors fabricated
using a) 150 nm Ti/350 nm Au and b) 150 nm Ti/990 nm Au at different RHs. To extract these data, IPMC was fixed at specific bent situation regarding the degree of deflection and the capacitance was measured as a function of humidity. As it can be deduced from Fig. 6a, 350 nm Au layer has lots of invisible cracks which does not give a good response at high deflections but it must be noted that a repeatable and reliable outputs were achieved for the IPMC with thick Au electrodes at all deflections. The capacitance behaviours as shown in these figures are somehow a nonlinear function of the electrode thickness. Bigger Au islands were formed on a sample with thicker Au electrodes which increases the capacitance values in Fig. 6b compared to Fig. 6a.

In order to explain the increase of capacitance with humidity in sample no. 2’s behavior, the model in ref [21] can be used. In this case, by increasing RH and diffusion of the H₂O molecules into the IPMC and changing the dielectric constant of the IPMC, a new εᵣ can be defined which in turn results in a new capacitance for the system. This happens through filling out the nano-channels inside the IPMC by H₂O molecules [22]. Normalized sensitivity of the capacitance to humidity for the range above 60% RH is calculated by Eq. (1) for both samples without any deflection.

\[ S = \frac{\Delta C}{\Delta RH} * \frac{1}{\varepsilon_{in \ 60\% \ humidity}} \]  

(1)

The results showed that the capacitor with thicker Au electrodes has much greater sensitivity (13.43%) than the one with the thin electrodes (1.022%). Another interesting phenomenon in Fig. 6b is that the capacitance decreases due to deflection at a specific RH (magnified part of the chart). This data can be used to calibrate capacitance vs. deflection in order to modify the RH reading values at different deflections (discussion on multi sensor/actuator system became earlier). This behaviour can be again described by the existence of cracks on the surface. At higher deflections, the electrode divides to higher number of metallic islands which finally result in the final capacitor. These parallel mini-capacitors will thus form a smaller C at higher deflection which is shown in Fig. 6b.

Fig. 7 illustrates the results of similar measurements on the sample fabricated using 150 nm Cr/350 nm Au electrodes. As it can be seen in this figure, this device also suffers seriously from the electrodes’ cracks even without any deflection and it can be concluded that the proposed contact cannot be a good choice for this application.

The results of the humidity measurements on how the best device (sample no. 2) responds to repeated cycles are shown in Fig. 8a. This test was performed under 10° deflections by increasing the RH from 40% to 90% and subsequently decreasing the RH to the primary value. It can be seen that the reverse behavior of the sample were exactly following the forward one. In order to extract the response time of this sample, a real time measurement of the device was investigated. Fig. 8b illustrates the result of an experiment in which the device confronts two changes in RH, after 20s from 40% to 65% and after 20 s later from 65% to 90%. The RH value stabilizes almost in 2 s but this saturation time for the IPMC is on the order of about 4 s. However, a sudden change from 90% to 40% RH as we have shown in Fig. 8a was taking much longer time on the order of 8–10 s.

4. Conclusion

A novel method for the IPMC fabrication is introduced in this article. It was experimentally shown that an IPMC system has the potential to be used as a multi-sensor of mechanical forces and humidity simultaneously by measuring its induced voltage and capacitance, respectively. The results showed that using a thin layer of Ti as an adhesion layer and surface treatment with roughening and oxygen plasma, adhesion between polymer and electrodes is improved, which is a suitable way to avoid the common problem of peel-off and cracks of the electrode. The fabricated IPMCs have been employed in manufacturing humidity sensors which can perfectly act at high humidity locations and even under different deflections. The sensors with thick Ti/Au electrodes proved to have high sensitivity which is fortunately not depending on the deflection of the IPMC membrane.

References


[22] H. Lei, W. Li, X. Tan, Encapsulation of ionic polymer-metal composite (IPMC) sensors with thick parylene: fabrication process and characterization results,
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