Micro actuator array based on ionic polymer with patterned self-assembled gold electrode

Marie Le Guilly[*], Chunye Xu[*], Minoru Taya[*] and Yasuo Kuga[**]

[*]Center for Intelligent Materials and Systems, Department of Mechanical Engineering,
[**]Department of Electrical Engineering,
University of Washington, Seattle, WA, USA, tayam@u.washington.edu

ABSTRACT

A new fabrication technique is proposed to create electrodes on thin ionic polymer membranes for micro actuator applications. The technique consists in plasma deposition of a thin (a few nm) allylamine coating on the membrane followed by stepwise assembly of Au colloids on the amine surface into a conductive electrode. Patterned gold electrodes can be created by using a stencil mask during allylamine plasma deposition. The influence of the allylamine plasma conditions on the electrode and the subsequent actuator is studied. A Flemion membrane (14μm) with a low power plasma allylamine coating and 10 sequential assemblies of Au colloids showed a fast, repeatable actuation at +/-1.5V.

Keywords: ionic polymer, self assembly, plasma polymerization, array, patterning, MEMS.

1 INTRODUCTION

Ionic polymer metal composite actuators (ion exchange membrane sandwiched by highly conductive compliant electrodes, see Figure 1) offer large deflection, fast, yet soft actuation, and a very good durability at low voltage in wet conditions. Therefore they can be used in pumps [1], valves and for manipulation in solution.
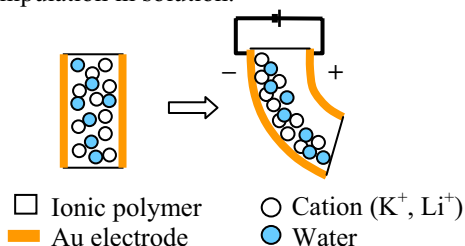

Figure1: Ionic polymer metal composite actuator

Previously, we reported [2] the fabrication of an actuator array based on a square of ionic polymer with a patterned electrode independently activating nine disk (diaphragm) actuators. To increase the spatial density of actuators we wish to scale down the actuator array. This requires a high resolution patterned electrode which cannot be achieved with chemical plating. In the more general aim of integrating ionic polymer actuators into MEMS, chemical plating is not suitable as an electrode fabrication technique because it requires lengthy immersions of the polymer in different ionic solutions with heating [3], which is not applicable if the polymer is already cast onto a MEMS. Zhou et al. used gold sputtering to create the electrodes of a Nafion microactuator anchored on a MEMS [4]. However, the large strain mismatch between the sputtered electrodes and the ionic polymer when the latter swells in solution is bound to create major durability issues. Therefore, a new fabrication technique yielding durable electrodes on ionic polymer with high resolution is very desirable. It would pave the way for the integration of ionic polymer actuators in MEMS, micro fluidic devices, and biochips.

Here, a new electrode fabrication technique is developed based on plasma treatment and self assembly (SA) of gold colloids. The fabrication scheme is presented in figure 2. Au-binding functional groups are created on the surface of an ionic polymer membrane by briefly exposing the membrane to an allylamine (AA) plasma which yields polymerization of AA (NH_2 functionality) on the surface.

By applying a mask on the membrane during the treatment one can pattern the allylamine, resulting in
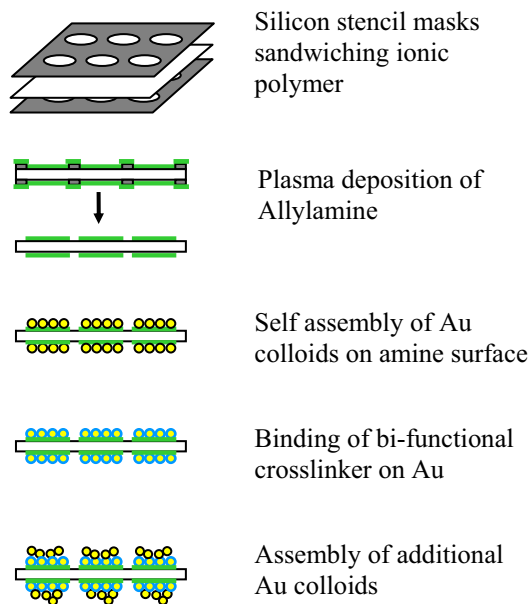

Figure 2: micro-patterned self assembled electrodes fabrication scheme.

patterned binding of gold in the following step. Immediately after this treatment, the membrane is soaked in colloidal Au followed by 2-mercaptoethanol or 2-mercaptoethylamine (MEA) and this process is repeated about 15 times (a technique developed by Natan's group [5]). After the surface water has evaporated, the Au colloid multilayer film changes from dark blue/black to shiny gold. With this technique, metal deposition is done in solution which results in no strain mismatch between the polymer and metal and thus, better durability. It is easily adaptable to microfabrication, and it allows high resolution patterning of the metal. Using this process, thin gold electrodes were created on an ionic polymer and actuation is demonstrated at +1.5V/-1.5V.

2 EXPERIMENTAL

2.1 Allylamine plasma polymerization

The plasma deposition is done on the surface of the dry ionic polymer membrane and so it will be affected once the membrane swells in solution (possible cracking and loss in coverage). In order to limit the expansion of the membrane after the plasma treatment, the ionic polymer membrane is pre-stretched before the plasma treatment. The membrane (Flemion, Asahi Glass Corporation, 14 μm thick, 1.8 meq/g, K^+ counter ion) is soaked in deionized water to reach a stable swelling state at room temperature and then the edges are clamped and the membrane is allowed to dry. By this process the polymer chains elongated by osmotic pressure in the wet state are forced to remain in this stretched condition in the dry state, and when the membrane is swollen again, it will not expand further.

NH_2 functional groups (which will bind to the Au colloids) are created on both sides of the pre-stretched membrane by plasma polymerization of allylamine. The plasma polymerization apparatus is similar to the one described in Ref 10. The allylamine monomer flows into the chamber via a needle valve. Allylamine is degassed by freezing-thawing 3 times before the polymerization experiment. The Flemion membrane is placed inside the chamber on a glass holder that allows coating of both sides of the membrane. The membrane is first exposed to an argon plasma for one minute at 15W, 150 mtorr. Then the membrane is exposed to the allylamine plasma with varying conditions (table 1) and an allylamine pressure of 150mtorr. Allylamine is allowed to flow in the chamber for 5 minutes after the plasma experiment for quenching. The allylamine coating is characterized by XPS. In order to create a gold pattern on the ionic polymer, the membrane may be sandwiched by stencil masks during the allylamine coating (figure 2). Silicon masks with micron size features can be made by photolithography and etching. The feasibility of patterning is proved here by the fact that the areas of the membrane that are covered by the glass holder during the plasma treatment do not show any gold assembly afterwards.

2.2 Stepwise assembly of gold colloids

The gold colloid solution is prepared according to Natan et al. [6]. After allylamine plasma treatment, the membrane is immediately soaked in 80 ml of the Au colloid overnight to let the colloid assemble on the amine surface. The gold monolayer on Flemion looks transparent blue. The membrane is thoroughly rinsed and soaked in 80ml 10mM 2-mercaptoethanol or 2-mercaptoethylamine for 10 minutes. The membrane is thoroughly rinsed again and put back in the colloid for 40 minutes. This sequence is repeated about 10 times or until enough gold has assembled. Finally the water on the surface of the membrane is allowed to evaporate and the coating turns shiny gold. The surface and cross section of the fabricated electrodes are observed by SEM-EDS.

2.3 Actuation

A strip (actuating length 3mm, total size 1x6mm^2) of Flemion with SA gold electrodes is tested as an actuator. It is previously soaked in 0.1N LiCl so that the cation inside is lithium. The electrodes are connected to a potentiostat (CH Instruments) and a 0.2Hz +1.5/-1.5V square voltage is applied. The actuation is recorded by a CCD camera.

3 RESULTS AND DISCUSSION

3.1 Allylamine coating

The allylamine polymer coating should be strongly bonded to the Flemion, it should be thin, and it should retain the most amine groups possible. The strong bonding was realized by cleaning and etching the surface of Flemion by argon plasma. A long exposure (5 minutes) to a 15 W Argon plasma was damaging the thin Flemion membrane so the duration was reduced to 1 minute. Different plasma conditions were used for allylamine polymerization. Low power continuous wave (CW) plasma and low equivalent power pulse plasma have been shown to yield polymers with well preserved monomer structure [7, 8]. Here, the amine group should be preserved in order for the film to bind with the Au colloids. Besides, it has been shown that polymer films deposited at low power tend to be less cross linked than the high power plasma polymers, and therefore they are more flexible [9] and they swell significantly in aqueous solution [10]. The swelling behavior of low power plasma polymer films may turn out to be very beneficial in the fabrication of the electrode as explained later. The conditions used here are summarized in table 1.

Table 1: Plasma polymerization conditions

#	Duty cycle	Peak power	Eq. power	duration
1	CW	22W	22W	2min
2	3ms/10ms	66W	20W	1min
3	CW	26W/7.5W	7.5W	10s/1min50s

The first sample (sample 1) was analyzed by XPS. Figure 3a) is the spectrum of the Flemion after Argon etching. The present elements are C, F, K, O and Si. C, F and O are the elements in Flemion, K is the counter ion in the Flemion and Si likely comes from surface contamination during pre-stretching where silicone rubber is used to clamp the thin membrane. Figure 3 b) is the spectrum of the membrane after allylamine polymerization. The only detected elements are C, N and O, suggesting that the membrane is completely covered by allylamine. This means that a brief (2 min) allylamine treatment is enough to
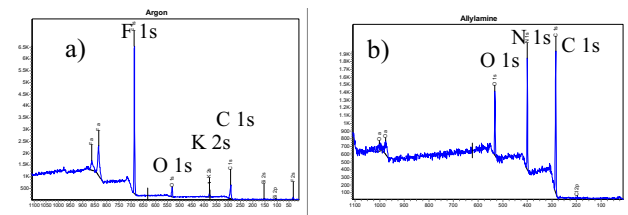

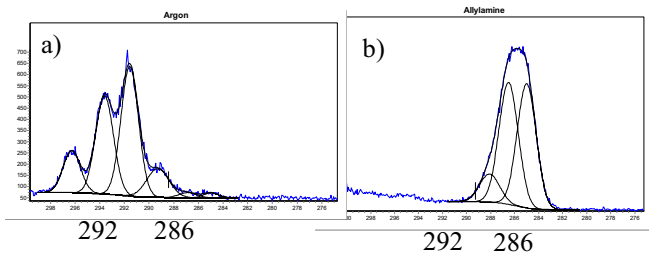Figure 3: XPS Spectra of Flemion after argon plasma a), and after allylamine plasma b).

Figure 4: C1s spectra of Flemion after argon plasma a), and after allylamine plasma b) (energy references in eV).

completely cover the membrane. The presence of a significant amount of oxygen in the allylamine film may suggest some air leaking in the plasma chamber, resulting in incorporation of oxygen in the polymer coating. Figure 4 shows the C1s spectra of Flemion after argon plasma, and after allylamine plasma. In the first case the C1s peak is centered around 292eV which is the binding energy of Carbon in Teflon (structure similar to that of Flemion). There are distinct peaks at higher energy, the peak at 294eV may be partly due to CF_3 groups in Flemion and there is probably also a contribution of potassium (K2p3/2 at 293.9eV and K2p1/2 at 296.7eV). Figure 4-b) is the C1s spectrum after allylamine polymerization, the broad peak is now centered at 286eV which is the binding energy associated with amine groups. This peak is composed of several peaks likely due to C-C (285eV), C-N (286eV), C-O (286.5eV) and to a lower extent amide (288.8eV). By limiting the leaks in the system, it should be possible to significantly decrease the amount of oxygen in the coating. Besides, by using a lower power CW or a pulse plasma, it should be possible to preserve better the monomer structure, resulting in a C1s peak rid of the C-O (286.5eV) component and higher energy components.

Based on all the above, two more samples where prepared. For these experiments, the allylamine monomer

was contained in a small tube with a high vacuum connector instead of the large spherical flask used in the first experiment, in order to significantly limit air leaking. One sample was prepared by pulse plasma (sample 2) and the other was prepared by low power (7.5W) continuous plasma. These samples are characterized in the following part in view of the SA Au films created on them.

3.2 Self assembly of Au colloids

After the first soaking in the Au colloid solution, all 3 samples showed strong assembly of Au, they turned dark blue. This suggests that the Allylamine plasma polymer films are very effective to bind Au colloids, probably more so than silanized glass substrates which appear pale red after the first Au layer and turn dark blue after several additional layers [11].

Figure 5 shows the Au colloids assembled on sample 2 after 4 soakings in the colloid solution and MEA. The spherical colloids are very distinct, they seem to assemble but not coalesce (figure 5-a)). Two issues arose with the use of MEA. First MEA appears to penetrate very easily in Flemion (maybe by an ion exchange process, MEA being positively charged in aqueous solution) and then to be released in the Au colloid solution in the following step, leading to precipitation of the colloid. Musick et al. reported this issue even for their glass samples but they were able to overcome the problem by an automated thorough rinsing [12]. The second issue was the very little binding of Au on MEA as opposed to mercaptoethanol. Wong et al. studied the orientation of mercaptoethylamine on Au and found that the molecule tends to adopt a gauche conformation to bring the positively charged amine closer to the gold surface [13]. This might indeed limit further Au binding. For samples 1 and 3, mercaptoethanol was used as cross linker between Au colloids. Au appeared to bind massively on mercaptoethanol and a resistance of about 50Ω (measurement in 2-point fashion with the probes 5mm apart) was obtained after 10 Au colloid layers for both samples 1 and 3. More work is underway to better understand the mechanisms of binding of Au and the different cross-linkers.

In sample 2, pulse plasma with an equivalent power of 20W was used to polymerize allylamine and no Au colloid seems to penetrate in the Flemion (figure 5). The same property was observed in sample 1 (not shown). On the other hand, in sample 3 (figure 6), a 7.5W continuous wave plasma was used and it appears that the gold colloids are able to diffuse through the coating in the Flemion. Zhang et al. reported that allylamine films prepared by low power continuous plasma were able to swell and showed DNA binding all throughout the film [9]. The allylamine coating on sample 3 is probably less cross linked than sample 2 and it is able to swell, therefore Au colloids are able to penetrate through the coating into the substrate. This characteristic is very beneficial towards making electrodes because this increases the gold contact area with Flemion.
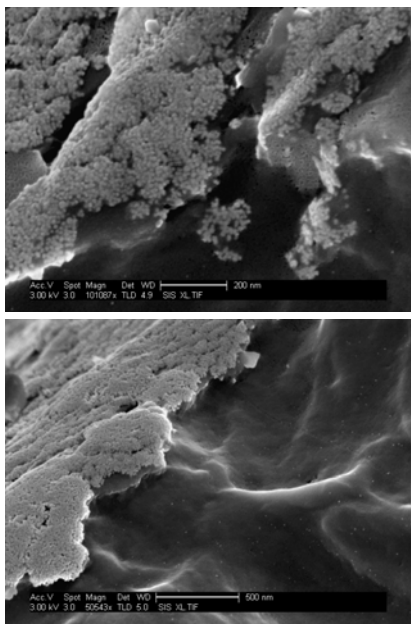
Figure 5: SEM micrographs of Au colloids assembled on Flemion sample 2 (cross section view), the cross linker is mercaptoethylamine (MEA).

Figure 6: Au colloids assembled on Flemion sample 3 (cross section view), the cross linker is mercaptoethanol.

3.3 Actuation

Sample 3 showed a fast, repeatable actuation at +/-1.5V (figure 7), the bending occurring mostly near the clamp probably because of the voltage drop along the sample. This actuation is remarkable given the resistivity of the electrode (still high relative to chemically plated electrodes [3]). Note that a voltage of +/-3V was necessary to get actuation of sample 1. The gel-like nature of the low power plasma (easily swollen) likely allows Au binding all throughout the coating and into the subsurface of the Flemion, insuring a better contact between the electrode and the membrane. The nature of the fabricated electrode (actually a collection of nanoelectrodes) makes it very effective at activating the polymer.
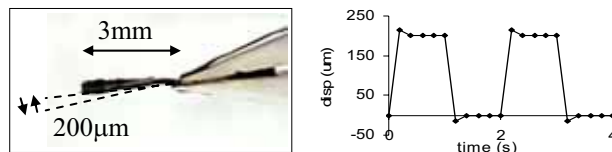

Figure 7: Flemion with SA gold electrodes, tip displacement (μm) vs time.

4 CONCLUSION

Low power plasma polymerization of allylamine and stepwise assembly of Au/mercaptoethanol appears effective to create electrodes on ionic polymer. This new technique is readily applicable for microfabrication and allows patterning of the electrode. The actuation obtained is very promising and suggests that the prepared electrodes, despite their relatively high resistivity, are very effective at activating the ionic polymer, behaving like a collection of spherical nanoelectrodes with very high capacitance.

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