Flemion based actuator for mechanically controlled microwave switch

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ABSTRACT

A microwave switch based on EAP presents several advantages. A switch based on Flemion is studied. Flemion a perfluorinated carboxylic acid membrane shows improved performance as actuator material compared with Nafion (perfluorinated sulfonic acid). Flemion has a higher ion exchange capacity and good mechanical strength. In order to get a good Flemion actuator, highly conductive soft gold electrodes with large fractal structure have to be deposited on the membrane. The impregnation reduction technique used for plating requires exchange of a gold complex and reduction by gradual sodium sulfite additions. K^+ shows the highest exchange ratio with the gold complex and reducing bath temperatures around 60°C with enough reducing agent present are shown to promote the growth of a gold fractal structure. The resulting material shows an actuation displacement with no relaxation, a key feature for switch applications. A simple mechanical switch based on a flemion actuator is prepared and tested as a microwave switch.

Keywords: electroactive polymer (EAP), ionic polymer metal composite (IPMC), Flemion, Nafion, actuator, microwave switch.

1. INTRODUCTION

Ionic polymer metal composite (IPMC) have been the object of great interest in the past years. Several polyelectrolytes have been demonstrated to show actuation properties. The most popular polyelectrolyte in this technology is the ion exchange resin Nafion made by Dupont[1,2]. The primary application of Nafion is fuel cell technology but the membrane has very good dynamic properties as IPMC actuator. Another polymer which also plays a major role in fuel cell technology is Flemion developed by Asahi Glass. This membrane has been studied as IPMC mostly by Oguro's group in Japan who achieved outstanding results in terms of actuation amplitude[3-6]. A very interesting characteristic of the actuation of Flemion compared with Nafion is the absence of relaxation, namely the deformation is stable as long as the voltage is applied. This allows to use Flemion actuators in switch applications where two stable positions are necessary. A possible field of application is the technology of microwave antennas for satellite based internet connections. Indeed these antennas use mechanical switches to switch connections on and off. A switch based on IPMC may be very simple and compact. It consumes very low power and may achieve similar performance as the current mechanical switches driven by small electromagnet.

In this work, a plating recipe to create flexible and highly conductive gold electrodes on Flemion is developed based on the impregnation reduction technique for Nafion developed by Fujiwara et al.[7]. The ion exchange behavior of Flemion is studied. Several plating conditions are tested and the resulting electrodes characterized. The actuation displacement and force of the prepared Flemion composite are measured and compared with the displacement and force of a Nafion composite. Actuation without relaxation is demonstrated. Finally a first flemion based microwave switch is tested. The switch gives good transmission and isolation but a more precise device with a more stable shape will be necessary to insure good repeatability.

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2. POLYMER METAL COMPOSITE PREPARATION

Deposition of the gold electrodes on Flemion is done according to the impregnation reduction technique[7]. In this technique a cationic gold complex $[Au(Phen)Cl_2]^+$ is first introduced in the membrane through ion exchange. The exchange of any cation inside the membrane by the gold complex will fully take place if the amount of gold complex in the exchange solution is sufficient to drive the exchange and if the affinity of the membrane for its present cation is not too high. To study the ion exchange, membranes containing $H^+/K^+/Na^+$ were each immersed in a gold complex solution and the content of gold complex ion and $H^+/K^+/Na^+$ was measured regularly for several hours.

In the second step of plating, the membrane is soaked in a reducing solution to reduce the gold on and near the surface of the membrane. The balance between the diffusion rate of the gold complex in the membrane and the permeation rate of the reducing agent determines the gold deposition pattern[7]. In order to design the plating route to get the optimum electrodes, recipes in which the reducing agent sodium sulfite was dispensed at different times and in different amounts were tried out and the resulting gold deposits were analyzed.

To get a low surface resistance and develop a large fractal structure, the impregnation/reduction cycle needs to be repeated several times.

2.1 Experimental

2.1.1 Gold complex ion exchange

Flemion H^+ or K^+ is soaked in water to reach a stable swelling state and roughened with sand paper to increase the surface area. It is sonicated for half an hour and washed in boiling water. In order to get Flemion with Na^+ counter ion, Flemion H^+ is soaked in 1N NaOH and then boiled in water. A sample (20x20 mm^2) of each membrane H^+/ K^+/ Na^+ is soaked in an aqueous solution (10^{-2} M) of the gold complex with stirring. Note that the Na^+ and K^+ samples are 70 micron thick whereas the H^+ sample is 145 micron thick so the amount of exchange solution needs to be larger in the case of the H^+ sample. Small samples of solution are taken at regular time intervals and analyzed with an inductively coupled argon plasma atomic spectrometer (ICP). The amount of gold complex entering and counter ion leaving the membrane is determined from the solution concentration change.

2.1.2 Reduction

Flemion exchanged with the gold complex is immersed in 40°C deionized water (reducing bath). Small amounts of 5wt% sodium sulfite solution are added gradually (reducing bath) and the temperature is ramped to 70°C. After 6 hours, the membrane is rinsed, boiled in acid and in deionized water. A cross section of the membrane is examined with the SEM and EDS.

2.2 Results and discussion

2.2.1 Gold complex ion exchange

The ion exchange profiles appear in figure 1. In the case of Flemion H^+ the amount of gold complex in the exchange solution is almost constant which means that almost no gold complex is absorbed. On the other hand the amount of proton in the solution increases a lot over the first 150 minutes. Since no gold complex enters the membrane it is impossible for the protons inside the membrane to leave (charge balance needs to be maintained in the membrane). Therefore the protons must come from another source. To check this point, a fresh gold complex solution was prepared and its pH was monitored over time (No membrane is present in this experiment). Without any membrane the pH of the gold complex solution decreased with time (figure 2). It appears that the gold complex is slowly hydrolyzed, which creates protons. F. Abbate et al.[8] showed that the gold complex is not stable in water. It looses one chloride first to form $[AuPhen(OH)Cl]^+$ and then the other chloride to form $[AuPhen(OH)_2]^+$. The dominant species in the solution after half an hour is $[AuPhen(OH)_2]^+$. The hydrolysis produces protons and therefore the pH of the solution decreases with time. In terms of ion exchange it seems that Flemion H^+ cannot be exchanged by the gold complex directly. This is mostly due to the weak acid property of Flemion. In order to exchange the protons in Flemion it is necessary to immerse it in a strong base with high concentration to offset the equilibrium towards dissociation of protons from the COOH groups. In the case of Flemion Na^+, the amount of gold complex in the solution decreases. The complex is penetrating in the membrane. However the amount of gold complex entering appears much smaller than the amount of sodium coming out. Sodium is probably not only exchanged by the gold complex but also and mostly by protons created in the gold complex solution. Finally in the case of Flemion K^+, the amount of gold complex entering is the largest. Yet the amount of K^+ coming out is smaller than the amount of sodium coming out. So the exchange ratio K^+/Gold complex is the largest. Like in the case of sodium the difference between complex going in and K^+ coming out suggests that some K^+ are exchanged by protons instead of the gold complex. In conclusion it appears that the bulky Na^+ (large hydration shell) is the easiest to remove from the membrane yet K^+ has the highest exchange ratio. This result is used in the plating route. After the acid treatment at the end of each plating cycle the membrane is soaked in KOH to introduce K^+. This maximizes the amount of Gold exchanged during the following impregnation step.

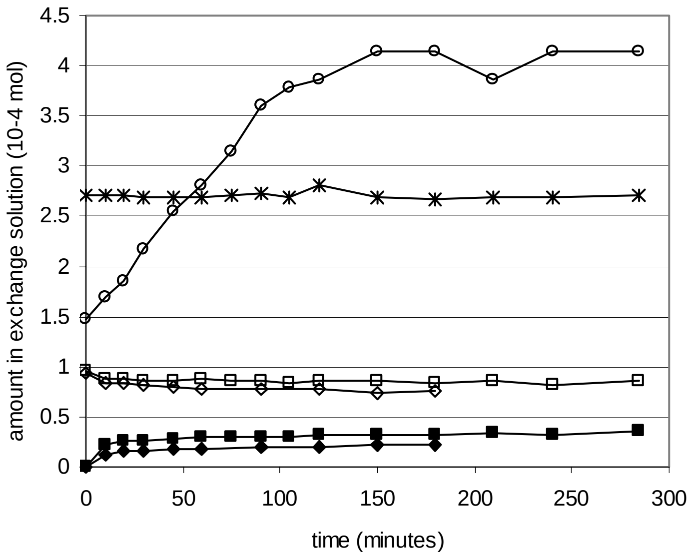


Figure 1: amounts of gold complex and counter ion in the exchange solution versus time. At t=0 the membrane is introduced in the exchange solution. Flemion H^+ (gold complex: star, proton: hollow circle), Flemion Na^+ (gold complex: hollow square, Na^+: black square), Flemion K^+ (gold complex: hollow diamond, K^+ black diamond).

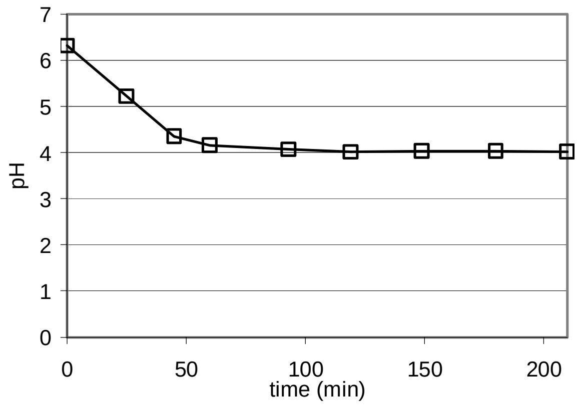


Figure 2: pH of a 10^{-2} mol gold complex solution versus time. At t=0 the complex is fully dissolved. Plain solution only, no membrane is present here.

2.2.2 Reduction

The plating parameters for different recipes are summarized in table 1 as well as the properties of the corresponding membranes. In cases 1 through 6, the temperature is slowly ramped after one and a half hour. In cases 7 through 9, the temperature is ramped after one hour and at a faster rate. Cases 5 and 6 only differ by the surface roughening treatment. In the first three cases the total amount of reducing agent added is very low. These cases yield a high surface resistance and a thin electrode. From the EDS scans across the thickness of the membranes (figure 3) it appears that some gold element remains in the center of the membranes after plating. By comparing these scans with the ones obtained in cases 4, 5 and 6 with a lot more reducing agent added, it appears the gold was probably not fully reduced in cases 1, 2 and 3.

Table 1: Plating conditions and properties of gold electrode

	Na_2SO_3 in solution at 40°C	Total Na_2SO_3 in the solution	Size of fractal structure (μm)	Surface Resistance of the electrode
1	12.6	12.6	0.5	MΩ
2	12.6	18.9	0.5	MΩ
3	12.6	25.2	1.5	10~100 KΩ
4	20	90	5	~1 KΩ
5	30	135	3.2	100~1000Ω
6	30	135	4.2	100~400Ω
7	15	135	4	1~10 KΩ
8	15	75	1	10~100 KΩ
9	30	150	1	~100 Ω

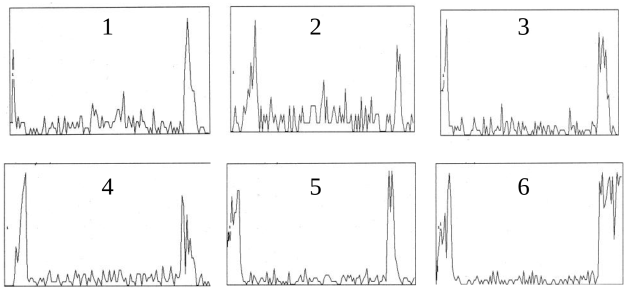


Figure 3: EDS scan for gold element across the thickness of the membrane in case 1 to 6 (see table 1).

The small amounts of reducing agent in cases 1, 2 and 3 were not sufficient to fully reduce the gold complex introduced in the membrane. From cases 5, 6 and 9, it appears that the amount of reducing agent in the solution at 40°C (first column) is a key factor to get a low surface resistance. Indeed these 3 recipes with the highest amount of Na_2SO_3 at 40°C yield a surface resistance in the hundreds of Ohms. The total amount of reducing agent used also influences the resistance as seen in the difference between case 1, 2 and 3. A limited amount of reducing agent at low temperature and convenient addition of reducing agent at higher temperature seems to promote fractal structure growth as seen in case 4 which yields the largest fractal structure (5µm). Higher temperatures (about 60°C) accelerate the penetration of the reducing agent in the membrane. If some gold complex remains in the membrane, it will be reduced inside and create a fractal structure. From cases 5 and 6 we see that even though a large amount of gold was already reduced at the surface at 40°C, the generous addition of reducing agent at higher temperature yields a large fractal structure. Recipe 6 has the best performance overall (low resistance and reasonably large fractal structure). In recipe 7 the limited amount of reducing agent at 40°C yields a higher surface resistance (low density of gold at the surface) but from the total amount of reducing agent finally added we would expect a very large fractal structure. However the fractal structure is only 4 microns. The difference between that recipe and recipe 4 is that a large amount of reducing agent is added at a higher temperature (over 60°C). That amount doesn't seem to translate into larger fractal structure. One hypothesis is that at 60°C the diffusion of the complex out is also promoted and a lot of reducing agent should be present to reduce the gold inside the membrane. In case 7 a smaller amount of reducing agent is present and the gold complex may diffuse to the surface instead of being reduced deep inside. Besides in this case high temperatures are reached sooner and the reducing agent is typically slow to penetrate in the membrane[7] so the diffusion of the gold complex may precede the penetration of the reducing agent. Case 9 also seems to support this hypothesis.

In conclusion to get a low surface resistance it seems preferable to add a lot of reducing agent at low temperature. This will promote the reduction of gold at the surface and yield a dense gold layer at the surface. To get a large fractal structure, a higher temperature is necessary to promote the penetration of the reducing agent inside. However high temperature also enhance the diffusion of the gold complex out of the membrane so it is necessary to have a lot of reducing agent present at these temperatures to reduce the maximum gold deep inside. The reducing agent should be allowed enough time at low temperature to start penetrating inside the membrane before the diffusion of the complex is accelerated.

3. ACTUATOR PERFORMANCE DATA

3.1 Experimental

Flemion (145 µm thick) gold composite is prepared according to the method discussed above and for comparison Nafion 117 gold composite is prepared according to a method mentioned elsewhere[9]. To measure the actuation displacement, strips (17mmx2mm) of the two membranes are set in a cantilever beam configuration vertically in deionized water and electrically connected to an electrochemical analyzer (CH Instruments). A square voltage +/-1.5V is applied with a period of 20 seconds in the case of sodium counter ion and 40 seconds in the case of tetraethylammonium (TEA) and tetrabutylammonium (TBA). The strips bend in response to the voltage and the displacement is recorded with a CCD camera. To measure the actuation force, strips (17mmx4mm) of the two membranes are set in a cantilever beam configuration horizontally in air and a force sensor is placed just above the strips at 3 to 4 mm from the fixed end. The actuators are freshly out of water and the remaining water is carefully wiped. The strips are electrically connected to the electrochemical analyzer. A square voltage +/-1.5V is applied with a period of 20 seconds in the case of sodium counter ion. In the case of tetraethylammonium (TEA) (Nafion) and tetrabutylammonium (TBA) (Flemion), a square voltage +/-2V with a period of 40 seconds is applied (note that it is necessary to apply a larger voltage in this case to get a good actuation of Flemion/TBA in air). The strips bend in response to the voltage and hit the force sensor. The output voltage of the sensor (related to the force applied) is input as external signal in the electrochemical analyzer. The analyzer software plots the current through the actuator and the signal from the force sensor in real time.

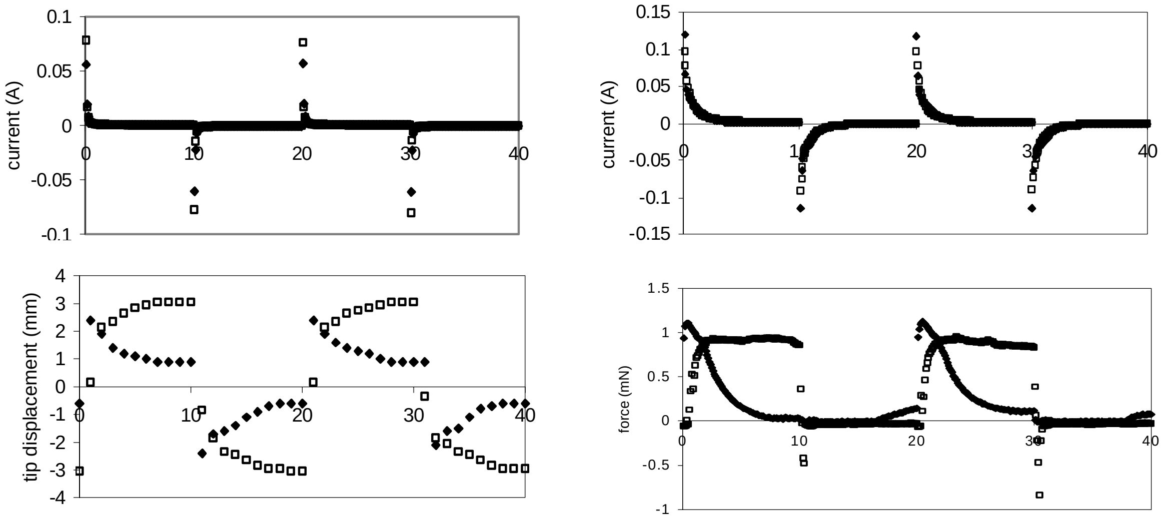


Figure 4: Right: current and displacement response of Nafion actuator (2mmx15mm, Na+ counter ion) (black diamond) and Flemion actuator (2mmx16mm, Na+ counter ion) (hollow square) in cantilever beam configuration in water. Left: current and force response of Nafion actuator (4mmx15mm, Na+ counter ion) (black diamond) and Flemion actuator (4mmx15mm, Na+ counter ion) (hollow square) in cantilever beam configuration in air. Voltage applied is 1.5V/-1.5V 10s/10s.

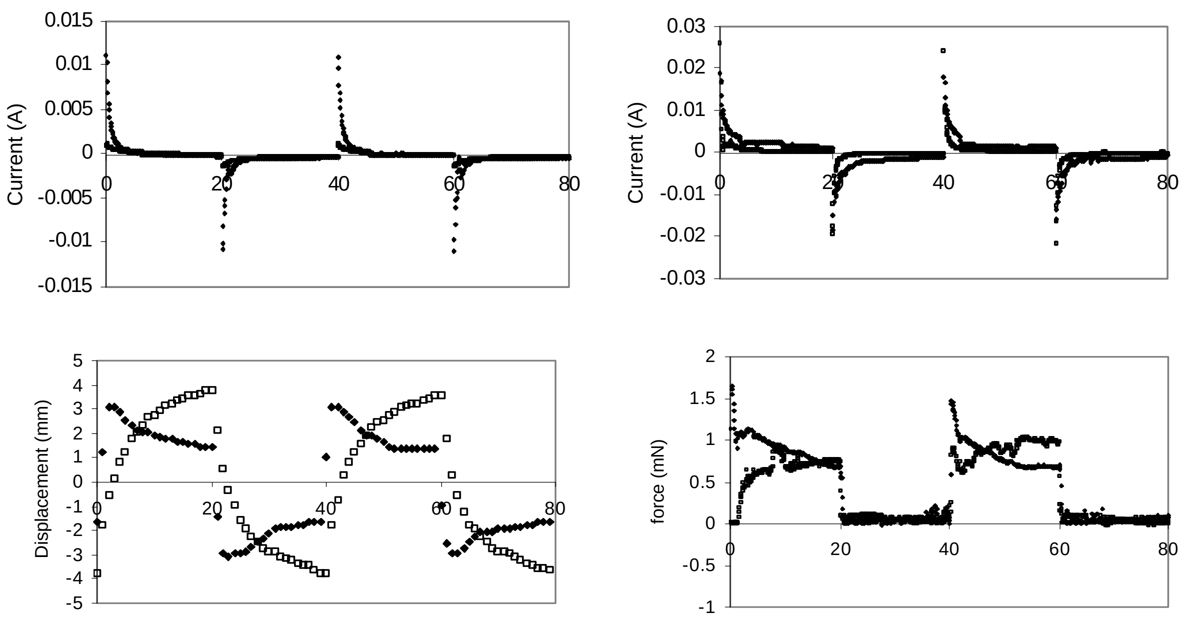


Figure 5: Right: current and displacement response of Nafion actuator (2mmx15mm, TEA counter ion) (black diamond) and Flemion actuator (2mmx16mm, TBA counter ion) (hollow square) in cantilever beam configuration in water. Voltage applied is 1.5V/-1.5V 20s/20s. The lower current is the Flemion case (around 1mA). Left: current and force response of Nafion actuator (4mmx15mm, TEA counter ion) (black diamond) and Flemion actuator (4mmx15mm, TBA counter ion) (hollow square) in cantilever beam configuration in air. Voltage applied is 2V/-2V 20s/20s. A higher voltage is necessary to get a force reading in the Flemion TBA case in air.

3.2 Results and discussion

The displacement and force response of the two membranes with sodium counter ion is given in figure 4. Nafion has a fast actuation to a maximum displacement and then it relaxes to a lower displacement. In terms of force, Nafion develops a large force in the beginning and then relaxes until it goes back to a smaller deformation and is no longer in contact with the force sensor. Flemion has an opposite behavior. It continuously deforms to a maximum displacement and maximum force. The actuation is fast in the beginning (2s) and then slows down and saturates, but no relaxation occurs. The currents in Nafion and Flemion with sodium counter ion are similar capacitive currents with the same time constant. The displacement and force response of the two membranes with TEA (Nafion) and TBA (Flemion) counter ion is given in figure 5. The bigger alkylammonium ions yield slower and larger deformations and smaller currents due to high resistance across the membrane. Nafion reaches a maximum deformation (in 2s) and maximum force and then relaxes. Flemion continuously deforms at slow speed to a large deformation. In air a larger voltage is necessary to actuate the Flemion TBA and get a force reading. The resistance across the membrane due to large radius of TBA ion in the polymer nanochannels is further increased when the membrane is not fully swollen with water. In conclusion we see that Flemion shows a different mechanical response than Nafion to the electrical stimulation. The carboxylic acid group and other properties of Flemion strongly affect ion movement as well as the electromechanical properties of the polymer network. In the sodium form, Flemion provides fast, stable actuation necessary for switch applications.

4. PRELIMINARY RESULTS AS MECHANICAL CONTROLLER OF MICROWAVE SWITCH

The microwave switch is a key component in the design of ground station antenna for future commercial high-speed satellite based internet connection. The current microwave switches are based on either mechanical or solid state devices. If many switches are required for the RF system such as in the phased array antenna, the power consumption, cost, attenuation and the PCB design become a major problem. EAP actuators are low cost and low power devices and they are suited for microwave application. The major drawback is a switching speed which can be up to 1 second. However, unlike military phased-array antennas which are designed to detect missiles, the internet in the sky antennas are used for tracking slowly moving satellites whose positions can be predicted. A low cost, slow microwave switch based on an EAP actuator is an ideal solution. The basic diagram of a microwave switch is shown in figure 6. The switch consists of a gap in the RF circuit section, a contact metal layer and an actuator on a driving board. The small gap on the microstrip transmission line (TL) as well as the contact separation distance determines the series capacitance which is related to the OFF state isolation level.

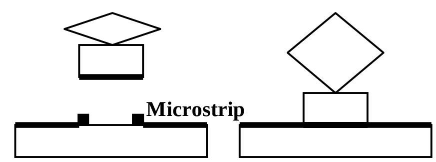


Figure 6: RF switch using EAP actuator

4.1 Experimental

A basic mechanical switch based on a Flemion actuator is designed and tested with a simple RF circuit. The first experimental setup is shown in figure 7. In this setup the switch was located under the board and was pushing a contact pad against the TL facing downward. In a new set up, the board is facing upward and the switch is above the TL (figure 8). The RF circuit consists of a copper line of width 0.75mm with a 1mm gap on a board made of Duroid 5880 (thickness 0.254mm, dielectric constant 2.20). The line is connected at each end to a network analyzer via coaxial cables. The network analyzer measures the transmission through the line as a function of frequency. The switch in the latest setup is shown in figure 8. A Flemion gold composite strip is set in a cantilever beam configuration. The fixed end is clamped between copper pads which provide the electrical connection. The beam bends in response to a low voltage and pulls a copper pad

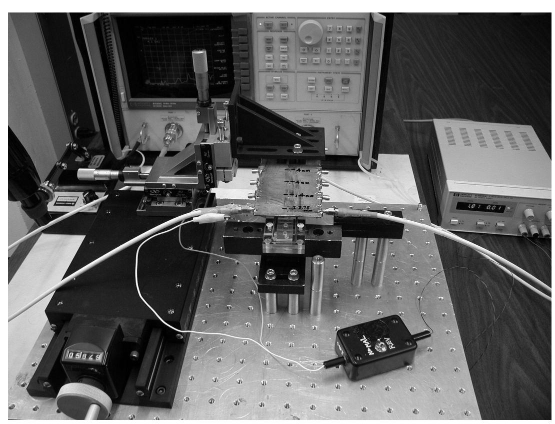


Figure 7: First setup. The RF circuit is facing downward. The EAP mechanical switch (small transparent box) is placed underneath. The black switch reverses the voltage polarity applied to the actuators.

(0.75mmx4mm) away from the TL in OFF stage. In ON stage the pad is resting on the TL. Actuator and electrical connections are put together in a small box made in acrylic plate. The device is connected to a power supply and the voltage applied is +/-1.5V. The counter ion in Flemion is sodium to get a fast actuation.

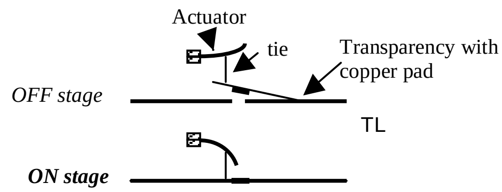
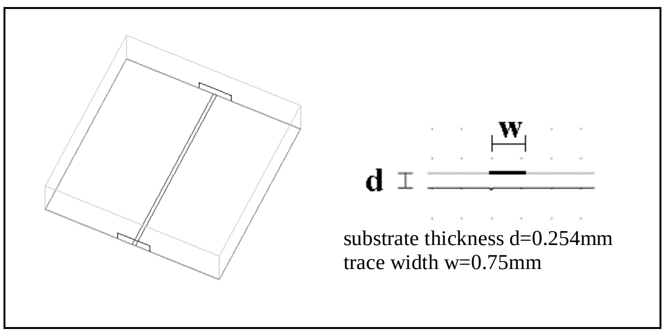


Figure 8: side view of the mechanical switch based on Flemion actuators

4.2 Numerical simulation

A numerical simulation of the electromagnetic problem is run in High Frequency Structure Simulator (HFSS) (ANSOFT). This is an electromagnetic finite element model. Three cases were modeled, the parameters entered are the same as the experiment, except the length of the copper pad (longer in the experiment). The first case (figure 9) is a continuous transmission line. The transmission is ideal according to the model. However the model does not predict how much contact force is necessary for the switch to match this continuous line condition. The second case (figure 10) represents the OFF stage when the contact pad is far from the transmission line. Note that in the model the pad is parallel to the TL which is not the case in OFF stage in the experiment. 1mm distance yields a very good isolation level -50dB at 2GHz. The third case (figure 11) is a model of the switch very close to the transmission line (2µm). The transmission is -2dB at 2GHz. Note that this is still far from the ideal case which means that the contact should be perfect to get a very good transmission. In the experiment this will require a perfect surface for the contact pad and perfect alignment of the pad with the line and a certain contact force may be necessary.



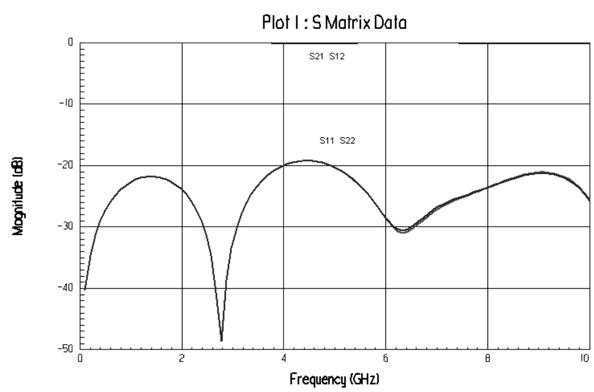
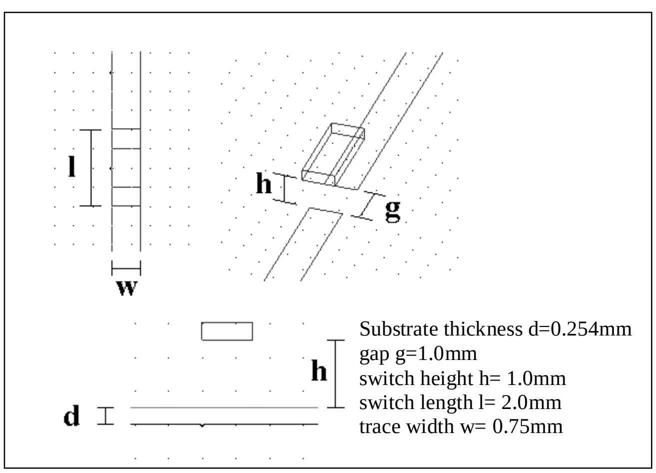


Figure 9: simulation of a simple transmission line (no gap). The transmission is ideal (0dB, whole frequency range, ideal ON stage)



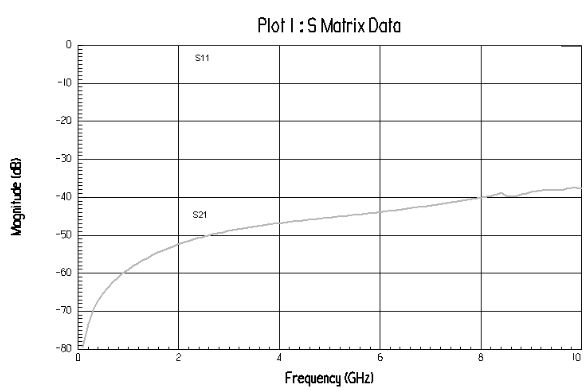


Figure 10: simulation of a transmission line with 1mm gap when the switch is 1mm above the line. This will correspond to the OFF stage (transmission is -50dB at 2GHz)

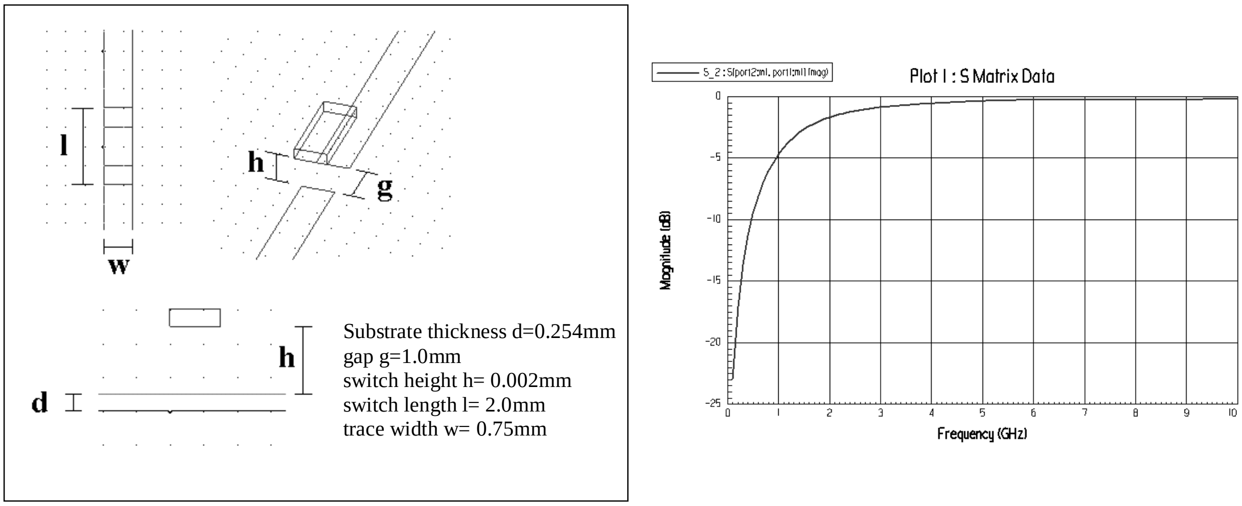


Figure 11: simulation of a transmission line with 1mm gap when the switch is 2 µm above the line. The transmission is -2dB at 2GHz.

4.3 Results and discussion

Transmission characteristics are given in figure 12. The frequency span is 0.05 to 10GHz. The insertion loss is below 1dB and the isolation is greater than 30dB. The length of the pad (4mm) yields a better transmission at low frequency (large overlap of the pad and the TL) compared with the model (2mm pad length) From previous experiments where the alignment of the copper pad was dependent on the actuator, it appeared that the precise alignment of the pad on the TL was absolutely necessary to get a good transmission. In this latest setup the alignment of the pad is independent of the actuator. The pad is fixed with respect to a flexing part which is fixed on the board. The actuator is only pulling on the flexing part. This insures good alignment of the pad with the TL and therefore good transmission in ON stage.

In conclusion, in this experiment, the actuator proved able to lift a flexing part with a copper pad and stay up for the duration of the experiment (several minutes). The switch gave good transmission and isolation but a more precise device with a more stable shape will be necessary to insure good repeatability. The actuator should be improved to be able to lift a heavier part (good contact force in resting state). Future work also includes coating of the actuator and durability testing. Ultimately, the goal is to simplify the design to make the switch more reliable while keeping a very high precision level. Another part of the work will be the extension to an actuator array and this may also influence the design.

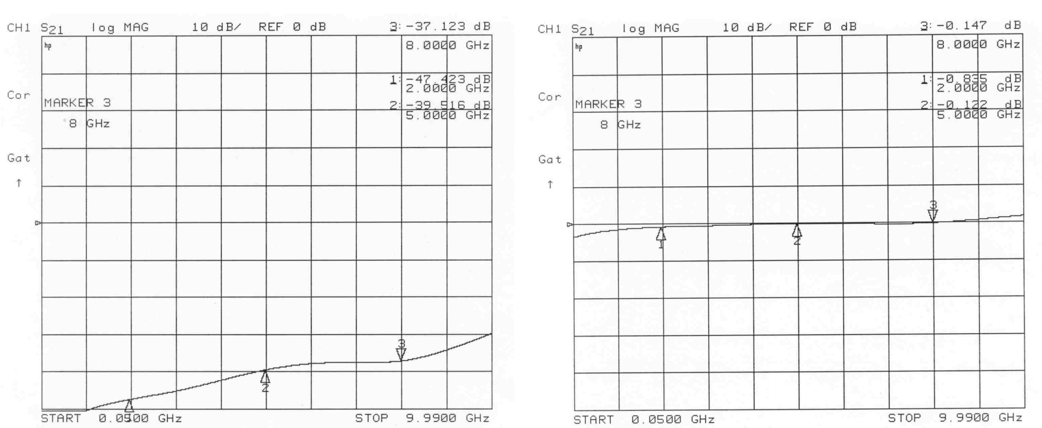


Figure 12: Left: transmission characteristic in OFF stage. Right: transmission characteristic in ON stage.

5. CONCLUSION

Flemion based IPMC actuators present the key advantage of stable deformation (no relaxation) and therefore are suitable for switch applications. A gold plating recipe based on the impregnation reduction technique is developed which successfully yields flexible, highly conductive electrodes on Flemion. In the ion exchange step, K^+ is shown to have the highest exchange ratio with the gold complex. The amount of reducing agent present in the reducing bath below and at 60°C seems to govern the growth of fractal structure. The resulting Flemion gold composite shows a fast actuation in the sodium form, with no relaxation. A simple mechanical switch based on a flemion actuator is prepared and tested as a microwave switch. The switch shows a good performance but a more precise device is necessary to insure high repeatability. The Flemion actuator shows very promising results but important issues like operation in air remain to be addressed for this material to play a role in microwave switch technology.

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