Fabrication and sensing
development of electroactive polymers

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Declaration

I hereby declare that I wrote the present dissertation with the topic: “Fabrication and sensing development of electroactive polymers” independently and used no other aids that those cited.

Ulm, July 2017

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Abstract

Ionic polymer-metal composites (IPMCs) are one of the most interesting types of “smart materials”. The “smart” denomination for these materials comes from the active deformation response of them to an electric field. Ionic polymers in any of their different forms are the basic concept in the field of smart actuating and energy harvesting function.

IPMCs have attracted lots of interest for a wide range of applications, from aerospace to medicine. These materials have been extensively used as actuators for many years but in order to improve their efficiency and applicability, a simultaneous sensing response should also be implemented in their function. The recent development of IPMCs as sensors-actuators has started up a whole new research field on self-sensing techniques and devices.

In this work, we present a new and improved self-sensing method for IPMC, which exhibits a series of advantages in comparison to other commonly employed methods. Two of the most usual self-sensing methods that have been used until now are mechanical-to-electrical transduction and surface resistance detection. Both of them have several drawbacks related to the cross-talk noise and the needs of especial modifications on the sample. With our technique, the IPMCs can work simultaneously as an actuator and a sensor without any interruption or interference between both operations. Additionally, our self-sensing technique does not require any extra sample modification of the IPMC to measure external disturbance on normal bending.

In addition, we have carried out a systematic study to reveal the mechanisms behind this novel self-sensing method. We have also performed simulation in order to optimize the system and find out which parameters improve the effective sensor
signal. Concerning the miniaturizing part, we have also investigated the minimum size required for the self-sensing operation of this improved technique.
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Chapter 1

Introduction to electro active polymers

Electro activity in polymers has given rise to a new field of research in science and medicine. In the last decade, the interest in the use of electro active polymers (EAP) as actuators has greatly increased, mainly motivated by the humans classical ambition of developing smart robots in the simplest, easiest and cheapest form.

The field of EAPs started up in 1880 when Wilhelm Röntgen examined the response of a rubber band under an electrostatic field [1]. The rubber band was fixed at one end and was attached to a mass at the other one. It was observed that the rubber length changed during charging and discharging process. In 1899, M.P. Sacerdote formulated a theory, based on Röntgen experiment of the strain response to electric field [2]. The discovery of piezoelectricity in 1925 put the spotlight on the EAPs and their promising applications [3]. Afterwards, for 50 years the elastic deformation on polymers was observed and studied under several other different stimuli including chemical, optical and magnetic [4, 5].

The EAPs have received a lot of attention specially in the new area of surgical technology, and as a consequence, several synthetic polymers that mimic the biological properties of muscles have been developed in the last 20 years [6].

EAPs are a type of smart materials that are sensitive to electrical and mechanical stimulation which means that they can respond to both electrical signal and mechanical forces. These materials can be essentially divided into two main subclasses,
based on their properties and functions: ionic and electronic electro active materials. Each type has distinguished properties and exhibits variable performance.

Electronic EAPs are basically built as dry polymer membranes with two metal layers on both sides. The thickness and shape of the polymer vary under applied voltage. These functions are mainly pertaining to strength of the electrostatic force between the two electrodes and the softness of the membrane. The electronic EAPs generally require high activation voltage and they normally show larger strain in comparison to the ionic one. Three main subgroups of electronic EAPs can be distinguished: dielectric elastomers, ferro electrics and electrostrictive polymers [7, 8].

One the other hand, the typical ionic EAP structure, consists on a polymer membrane swelled in ionic solution and sandwiched between two metal electrodes on either side. In this case, the electric field redistributes the ions in the polymer lattice in a way that leads to global deformation of the whole specimen [9]. Ionic EAPs can be divided into different subgroups, depending on the nature of the polymer: Ionic polymer gel (IPG), Ionic polymer metal composite (IPMC), Conductive polymer (CP). Both IPGs and IPMCs are made of polymers with polyelectrolyte units turn to the charged units in aqueous solutions. These two systems are similar in many aspects [10] [11]. However, in IPG systems, the exchange of electrolyte take place between the polymer and the surrounding medium but for IPMCs the ions and water molecules just flow inside the polymeric micro channel without any mass exchange to medium. This principle allows IPMCs to have similar working capabilities both in wet and dry conditions in contrast to IPGs. Finally, the CP groups are typically organic polymers that conduct electricity. These components are normally semiconductors with distinct functioning and properties [12].

The focus of this research has been on studying IPMCs for their actuating and sensing. IPMC materials are able to convert electrical energy to kinetic energy in a reversible and repeatable way. The efficiency of this process and their actuating properties strongly rely on the applied electric signal. At low voltages (less than 5 volt), the free ions inside the polymeric film react to the external electric voltage by moving in the direction of the field from positive to negative electrode. This movement causes an osmosis pressure which leads to the bending of the soft polymer structure. Higher voltages can hydrate the water in the medium and disturb the
movement of ions. The Operation of IPMCs is also strongly related to the frequency of the applied AC electric field. As the ions are heavier than electrons, the movement of the ions dominates the actuating of IPMC especially in the frequency range under few hertz. In the high frequency range, ions cannot follow the fast variation of the AC electric field and they mostly behave as immobile charged particles. In this range, only the electrons contribute to the electrical properties of the sample without any actuating effect[13].

IPMCs should not be considered just as simple actuators but also as smart actuators thanks to the real time feedback control enabled by their sensing capacities. In fact, one of the most interesting features of IPMCs is capacity to work both as actuators and sensors. IPMCs can also be used as position or force sensors when exposed to mechanical force. This force rolls up the mobile cations inside the polymeric membrane near the electrode and generates an inward current as response to deformation[14]. In order to be detected, this inward current needs to be amplified by a proper method as it is much smaller than the driving signal (100 times) induced in the system.

The concept of 'inside sensing' unbuttoned a new research field of 'self-sensing IPMCs'. Different categories of self-sensing IPMCs have been developed depending on the particular property of sample(surface resistance, capacitance or bulk resistance) whose change is analyzed during the mechanical actuating. One way to implement the self-sensing operation is by dividing the IPMC strip into two separate parts, actuator and sensor[15]. The driving voltage is applied on the actuator part of IPMC, which mechanically moves the attached sensor part. The force the on sensor part causes an ion flow inside the polymer membrane and creates a short current can be used as sensor signal. In this system, the ion movement happens at same frequency as the actuating voltage, and therefore, since the sensor and actuator signals share the same frequency and are close together, they can be affected by each other due to crosstalk noise. To avoid this problem, a non-conducting shield between the two separate parts should be incorporated.

The efficiency of the isolation from capacitive and conductive coupling between the two signals can be improved by increasing the width of the non-conducting shield. One of the most common ways that have been devised to implement this shielding part is by patterning the surface of IPMC strip. Unfortunately, the patterning of the
sample in three different parts reduce the active actuating area of the sample and makes even more difficult to miniaturize the IPMC with a wide range of applications, as desired.

In this work, we have developed a novel method to effectively separate the detector signal and driving signal without having to pattern the sample. Here, frequency separation has been used instead of physical strip separation. As explained before, the electric behavior of IPMCs depend on the frequency of AC electric field applied: ionic contribution prevails at low frequencies, while in the high frequency range, the main contribution comes from electrons. Considering this, we have developed a new self-sensing method, free of any distortion between the sensing and actuating operation, and without the need of any further modification (patternning) of the polymer. This method is essentially based on the successful frequency separation of the driving and sensing signals by using an electrical circuit supplied by two function generators, which allows us to sweep different frequencies, and a lock-in amplifier to amplify the signal [16].

The other focus of this research has been to fabricate IPMCs by chemical and physical methods and to analyze their advantages and disadvantages by characterizing and comparing performance of samples prepared by both routes.

This thesis has divided into six chapters:

Chapter 2 explains the main theory of the chemical process takes place inside the polymer during the operation of the IPMC. The mathematical model to formulate the IPMC functioning comes in two different approaches, electrostatic and electromechanical. Under these two conditions, we have first studied the water uptake by ionized polymer and then the sample performance under an electric field.

Chapter 3 contains details about the IPMC fabrication and characterization by both chemical and physical methods, with special stress on the advantages and disadvantages of each method. The morphology of the film has been characterized by scanning electron microscopy (SEM) and the interface boundaries and the diffusion zone of metal particles in polymer has been studied by transmission electron microscopy (TEM). The patterning on polymer in physical method and metal deposition on patterned polymer has been tried by several techniques. Plasma treatment and electron etching are two methods to improve the polymer metal adhesion which
both have been studied in this chapter.

The study of the IPMC actuating properties is the subject of chapter 4. The sample functioning and its dependence on the voltage and frequency are described at the end of this chapter.

The sensing aspect of the IPMC is described in chapter 5. The combination of the actuating and sensing capacities by distinct methods is also explained in detail in this chapter.

Finally, simulations have been developed in chapter 6 in order to optimize the whole process and the obtained results have been compared with the experimental ones as well. The last part of this chapter focuses on the miniaturizing procedure on IPMC samples.
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Introduction to electro active polymers


Chapter 2

Theory and model

This chapter presents the theory and mathematical models behind the IPMCs performance. The IPMC sample in general form is a polyelectrolyte film, which can specifically exchange ions from encompassing fluid with their own particular unique ions[1]. The properties of dry IPMC extraordinary changes, after ionic fluid absorption. The distinct properties of polymer under dry and wet conditions is explained in first part of this section. Next, the role of electric field in electromechanical reaction of IPMC and bending mechanism will be explained. Furthermore, the general equations and relations to speculate required materials for sample preparation are described in this chapter.

Nafion is one of the most common and commercially available ion exchange membranes. This polymer is consisted of a copolymer backbone of tetra fluorocarbon with perfluoro vinyl pendant chain terminating in sulfonic acid groups.

The fluorocarbon is hydrophobic and the ionic unit with sulfonic acid is hydrophilic. Therefore, these two segments are incompatible and Nafion has a phase separated morphology because of discrete hydrophobic and hydrophilic regions.

Figure 2.1 shows Nafion structure with possible position of rotation around fluoride chain, that creates the clusters and micro channels in IPMC structure [2].

When the Nafion expose to water, its ionic groups tend to form clusters in the three-dimensional polymer structure. These firmly localized ionic groups in Teflon region make completely interconnected micro channel filled by water. IPMC sample created by any available technique needs to immerse in ionic liquids at the final
fabrication step. At this step, the hydrogen, H in sulfonic groups substitutes by Mg, Na or K ions from the ionic fluid. Then the polymer membrane is filled by these cations which is encompassed by water molecules. Under applied voltage they move in micro channels in direction of electric fields[3].

Fig 2.2 shows schematic micro channels and cation fluid under voltage.

To characterize the IPMC function, two approaches must be considered: First, polymer investigation without voltage at extended shape by ionic fluid and second, effect of electric field on properties of polymer. Both subjects are demonstrated in fig 2.2 and will be clarified by details in the following sections.
2.1 Electro static approach

As specified before, Nafion polymer structure is comprises of fluorocarbon back-
bone and cluster networks incorporates fixed anions (sulfate groups) and replace-
able cations (H) by (Mg,Na,K) from the ionic liquids. At hydrated state, in absence
of electric field, these cations (Mg,Na,K) can diffuse inside the micro channel and
will disperse in all clusters to minimize the Gibbs free energy. For electro static
approach, first characteristic parameters of polymer membrane will be introduced.
The pressure in the clusters due to osmotic and electro static forces will be formulated. Finally, by using the relation between internal pressure and elastic stress,
Young modulus can be calculated.

2.1.1 Characteristic parameters

One important factor to characterize an ion exchange membrane is its content of
ions which normally defines by equivalent weight $EW_{\text{ion}}$ [4].

For Nafion 117 $EW_{H^+} = 1100$ g per mole $SO_3^-$ when the polymer is in original
form by $H^+$ as cation. This definition extends for various cations as follows:

$$EW_{\text{ion}} = \frac{(EW_{H^+} - 1.008 + FW_{\text{ion}})}{SF}$$  \hspace{1cm} (2.1)

Where $FW_{\text{ion}}$ is formula weight for replaced cation and SF is the scaling factor
which can be defined by equation 2.2.

$$SF = \frac{\text{mass(dry ionomer)}}{\text{mass(dry IPMC)}} = 1 \text{ (for polymer without electrodes)}$$  \hspace{1cm} (2.2)

The cation content was calculated before by equivalent weight and now is impor-
tant to determine the anion concentration as well. The ion concentration is the
basic parameter in IPMC function and unequivocally relies on the volume of water
absorbed by the membrane. The volume of uptake water is called water content
(w) and defines as proportion between volume of absorbed water and volume of dry
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polymer.

\[ w = \frac{V_{H_2O}}{V_{dry}} \]  \hspace{1cm} (2.3)

From these two parameters, \( EW_{ion} \) and \( w \), the molality of anion in sample can be calculated by:

\[ m = \frac{\rho}{EW_{ion}w} \times 10^3 \]  \hspace{1cm} (2.4)

When \( \rho \) is the density of the dry sample. This molality calculated for moles of the anion in IPMC sample per liter of water content. To convert this value to moles of anion per cubic meter of swelled sample, equation 2.5 should be used.

\[ C^- = \frac{w}{1 + w} \times 10^3 m \]  \hspace{1cm} (2.5)

Here, \( C \) is ion concentration for anion. Total ion concentration for mole anion and cation per mole water is expressed by:

\[ C = 18 \times 10^{-6} (C^+ + C^-) \times \frac{1 + w}{w} \]  \hspace{1cm} (2.6)

Where \( C^+ \) is cation concentration measured for each experiment. Base on total concentration, total molality \( v_m \) for anion and cation can be calculated by equation 2.7. The total molality and ion concentration are the definitive parameter on osmotic flow in clusters.

\[ v_m = 10^3 (C^+ + C^-) \times \frac{1 + w}{w} \]  \hspace{1cm} (2.7)

2.1.2 Osmotic force

In IPMC structure, the clusters are semipermeable membrane isolated two solutions contain various cation concentration. For polymer, osmotic pressure originates from the distinction in chemical potential between two states. Two states are free water
and water in clusters with known ion concentration\[5\]. The chemical potential of water $\mu$ in membrane is computed by:

$$\mu^w = \mu^w_0 + 18(10^{-6}p - 10^{-3}RT\phi_m)$$

(2.8)

Where, $p$ is the water pressure in pascal, $R$ is universal gas constant and $T$ is absolute temperature. Here, $\phi$ is practical osmotic coefficient which characterizes the deviation of a solvent from ideal behavior and relies upon molality $m$.

The osmotic pressure $\Pi$ is the minimum pressure which needs to be applied to a solution to prevent the inward flow of water across a membrane. It can be computed as:

$$\Pi = \frac{v_m p R T \phi}{E W_{ion^w}}$$

(2.9)

### 2.1.3 Electrostatic force

This section consider electrostatic forces in clusters when no voltage is applied to the sample. Each cation - anion pair can be considered as a dipole. The polymer comprises of cation $H^+$ and anion $SO_3^-$ in dipole shape disseminated over the clusters. When the sample absorbs ionic liquids, $H^+$ will be replaced by $Na^+$. Also water molecules interfere dipole shape and dipole-dipole collaboration force [6]. The shape of a dipole $Na – SO_3$ structure is shown by fig 2.3.

![Dipole structure](image)

*Figure 2.3: Dipole structure*
Based on the water uptake volume, dipole electrostatic interaction redistributes the cations and changes the pressure in each cluster. To compute this pressure, dipole density $\rho$ is required parameter which calculates by equation 2.10. In this equation, spheres of radius $\alpha$ for dipole is expected and charge density $q$ is distributed in cluster zone.

$$\rho = \alpha q$$

(2.10)

Here, $\alpha = \alpha(w)$ is the effective dipole radius identified with water uptake $w$. By this presumption, the pressure produced by electro static force in a cluster can be calculated by integrating the coulomb force on a sphere between one dipole and all other dipoles distributed around.

$$P_{DD} = \frac{1}{3K_e}(\frac{\rho F}{EW_{ion}})^2 \pm \frac{\alpha^2}{w^2}$$

(2.11)

For this dipole-dipole pressure, $K_e$ is the effective electric permittivity and $F$ is Faraday’s constant. This pressure over the cluster area generates the force and diffuses the ions in membrane medium. The total pressure in every cluster is the summation of osmotic and electrostatic pressure:

$$P_c = \Pi + P_{DD}$$

(2.12)

### 2.1.4 Stiffness and Young modulus

In two previous sections, osmotic pressure and dipole-dipole interaction pressure in absence of electric field were introduced. These two parameters are firmly related to ion content $EW_{ion}$ and water uptake “w” by the polymer.

A dry polymer in the aqueous medium, absorbs water until the total pressure in the clusters is in balance with the elastic stress[7]. Assuming a spherical shape of clusters the radial stress at an initial distance of $r_0$ from the cluster center is expressed as:
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\[ \sigma_r(r_0) = -P_0 + K\left[\left(\frac{r_0}{a_0}\right)^{-3}\left(\frac{w}{w_0 - 1}\right) + 1\right]^{-\frac{1}{3}} \] \hspace{1cm} (2.13)

Where \( P_0 \) is initial pressure of bare membrane which can be computed based on primary volume of cluster and \( K \) is effective stiffness depending on cation sort and concentration. The parameters \( r_0 \) and \( w_0 \) are initial values for radius of cluster and water content before ion replacement.

Water absorption stop when \( r_0 = a_0 \) and \( w > w_0 \) then:

\[ \sigma_r(a_0) = -P_c \] \hspace{1cm} (2.14)

In this condition, clusters have maximum size and water uptake is highest value. The effective stiffness by using equation (2.13) computes as:

\[ K = P_c(1 + \frac{w}{w_0 - 1})^{\frac{1}{3}} \] \hspace{1cm} (2.15)

This effective stiffness is calculated for pure polymer but the impact of metal electrode on the stiffness must be also incorporated. The value should consider the type of utilized metal and thickness. Assuming a 20-30 \( \mu \)m metal layer on both surface of polymer and 1-10 \( \mu \)m penetration inside the polymer, the general stiffness of composite is obtained by averaging strain \( \varepsilon \) and stress \( \sigma \) over the strip.

\[ \varepsilon_{IPMC} = f_{MH}\varepsilon_M + (1 - f_{MH})\varepsilon_B \]
\[ \sigma_{IPMC} = f_{MH}\sigma_M + (1 - f_{MH})\sigma_B \] \hspace{1cm} (2.16)

Where \( f_{MH} \) can be state as \( f_{MH} = \frac{f_M}{1+w} \)

In formula, M denotes metal and B bare membrane and \( f_M \) is volume fraction of coating in dry condition based on the subsequent equation:

\[ f_M = \frac{(1-SF)\rho_B}{(1-SF)\rho_B + SF\rho_M} \] \hspace{1cm} (2.17)

As stated earlier, \( \rho \) is the mass density and SF is the scaling factor and \( w \) denotes the water content.
The Young modulus for sample is the stress to strain ratio and can be calculated by using equation 2.16. For the Nafion polymer the Young modulus is related to stiffness of sample while $Y = 3K$. The stiffness is the resistance of an elastic body to deformation and is defined as force to displacement ratio. By applying the electric voltage to IPMC, voltage to curvature ratio is identified by the stiffness. For each sample the Young modulus can be calculated based on ion type and initial condition [6].

### 2.2 Electrodynamic approach

When an IPMC strip in a hydrated state is subjected to an electric field, the initial cations distribution inside the membrane turn to new dissemination. This process happens because the cations on the anode side drive out of the anode boundary clusters while the clusters in the cathode side supply with additional cations. This redistribution of cations under applied potential can be explained by the coupled electrochemical equations. This effect is considerable in two boundary layers near both electrodes. The change in ion concentration affects the sample stiffness and result into a fast bending motion towards the anode and a slow relaxation motion toward the cathode after the fast bending. To explain all reactions caused by the electrochemical potentials (chemical concentration and electric field gradients), governing coupled equations are necessary [8].

The total flux consists of the cation migration and the solvent transport can be calculated by considering some assumptions: First, the anions are fixed in the polymer backbone then the ion migration considers just the cations. Second, the water flux is slow process then the water diffusion is generally depended on position, not on time. Based on these two assumptions total flux under the electric field is:

$$J_i = -\frac{C_i d_i \partial \mu_i}{RT \partial x} \quad (2.18)$$

When “i” denotes each effective species, d is the diffusion coefficient and $\mu$ the chemical potential and C the concentration is calculated in the previous sections.
The variation of chemical potential is the most effective parameter in total flux and is given by:

\[
\mu = \mu_0 + RT \ln \left( \frac{\gamma^+ C^+}{\gamma^0 C^0} \right) + F \varphi
\]  

(2.19)

The value of \( \mu_0 \) is initial chemical potential and \( \gamma \) the chemical affinity of species. In this equation \( F \) is Faraday’s constant, \( R \) is the gas constant, \( T \) is the absolute temperature and \( \varphi \) is electric potential.

The relation between the ion flux under electric field and the gradient of ion concentration can describes the entire procedure. This relation is known as Poisson-Nernst-Planck equation[9].

### 2.2.1 Poisson-Nernst-Planck equation

The Poisson-Nernst-Planck equation is an express of mass conservation when ion concentration gradient change due to electric field. The conservation equation in general state consists of three terms of migration, convection and diffusion in polymeric matrix [10].

\[
\frac{\partial C}{\partial t} + \nabla \cdot (vC) + (\nabla \cdot J) = 0
\]  

(2.20)

In this equation \( v \) is the water velocity.

In a very good approximation, ionic liquid can be modeled as a fluid then \( \nabla \cdot v = 0 \). In this case, the convection term in equation 2.20 only depends on the concentration gradient and the velocity of solvent. Additionally, the diffusion is remarkable just in the direction of electric field and the Poisson-Nernst-Planck equation for IPMC expresses as:

\[
J^+ = -d^+ \left( \frac{\partial C^+}{\partial x} + \frac{C^+ F}{RT} \frac{\partial \varphi}{\partial x} + \frac{C^+ V}{RT} \frac{\partial \rho}{\partial x} \right)
\]  

(2.21)

where \( V \) refers to the volume and \( d^+ \) is the ionic diffusion coefficient.
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The general electrostatic equation when $D$ is electric displacement and $E$ electric field and $\kappa$ electric permittivity is expressed by equation 2.22:

\[
\frac{\partial D}{\partial x} = (C^+ - C^-)F
\]

\[
D = \kappa E
\]

\[
E = -\frac{\partial \varphi}{\partial x}
\] (2.22)

By combining equations (2.20) to (2.22) we obtain:

\[
\frac{\partial}{\partial x}\left\{\frac{\partial (\kappa E)}{\partial t} - D^+\left[\frac{\partial^2 (\kappa E)}{\partial^2 x} - \frac{C^- F^2}{\kappa RT}(\kappa E)\right]\right\}
\]

(2.23)

This equation is able to describe behavior of IPMC by time and position variation under the electric field.

2.3 Strip displacement

The strip displacement calculation considering the IPMC sample as a cantilevered strip is presented in the following part [5].

As mentioned before, the cations redistribution in IPMC clusters are changed by electric field which changes the strain value of sample. The changing of strain is proportional to the change of water uptake and results into the bending. The rates of variation for sample strain is called as eigenstrain and is calculated by:

\[
\dot{\varepsilon}_v = \frac{\dot{w}}{1 + w}
\] (2.24)

The eigenstrain and water uptake are volumetric values in three dimensions but for IPMCs the main movement is in one direction along the thickness. Then the effective eigenstrain in $x$ direction is expressed by:

\[
\dot{\varepsilon}_{v^*}(x, t) = \frac{1}{3}\dot{\varepsilon}_v
\] (2.25)
For the free end of IPMC strip, the rate of displacement \( \dot{u} \) is related to maximum strain rate \( \dot{\varepsilon}_{\text{max}} \) and is computed by equation 2.27.

\[
\dot{\varepsilon} = \frac{2H \dot{u}}{L \tilde{L}} \tag{2.26}
\]

Here, \( 2H \) is the thickness of the hydrated sample and \( L \) is the length.
Bibliography


Chapter 3

Fabrication and characterization

The focus of this chapter is fabrication and characterization methods of IPMC samples. It is divided into three main parts: First, principals of experimental techniques such as electron microscopy, surface profile meter, laser confocal microscopy, contact angle measurement and the electro-mechanical test are explained. Second, the properties of required materials consist of specific polymer and chemical compounds for metalization process are described. Finally, the fabrication procedures for the IPMC sample by two different approaches, chemical and physical, are presented. For each approach, the fabricated samples are compared by characterization results.

3.1 Experimental techniques

The characterization techniques in this section reveal information about morphology of sample and interfaces. Furthermore the adhesion properties related to surface energy and penetration depth of deposited material can be investigated with same specific techniques. All this methods are helpful to study the sample preparation during different stage of fabrication process.
3.1.1 Electron microscopy

The optical microscope generally uses visible light with a certain range of wavelengths. Electron Microscopes are developed due to the limitations of light microscopes which are restricted by the nature of light. To see the fine details of small structure, a beam of highly energetic electrons examines the objects. This examination can yield information about the topography (surface features of an object), morphology (shape and size of the particles making up the object), composition (the elements and compounds that composed the object and the relative amounts of them) and crystallographic details (how the atoms are arranged in an object).

Scanning electron microscope (SEM) uses an electron beam to illuminate the sample. The beam is produced by electron gun installed in the top of the microscope [1]. The electron beam goes through a vertical path in the microscope, which is held in a vacuum. The control of path and shape of the beam are possible by electromagnetic lenses. The beam finally is focused on the sample and collided with electrons or nucleus of the atoms. Different signals produce based on beam-sample interaction. The principle of produced images in SEM are based on three signals: secondary electrons, backscattered electrons and X-ray signals. When the electron beam scatters from the specimen, high-energy backscattered electrons generate. The beam in interaction with an atom loses energy and emits low-energy secondary electrons, light emission or X-ray emission. All signals carry information about the properties of the specimen surface, such as its topography and composition. Detectors for each type of signals are placed under the microscope in proper positions to collect them.

Transmission Electron Microscopy (TEM) is a characterization technique based on electron beam-sample interaction. The emitted electrons by the source are focused and magnified by a system of magnetic lenses. Afterwards the electron beam passes through a thin layer of sample and reach to the objective lens [2]. The main function of the objective lens is to focus the transmitted electron from the sample into an image. Before the image screen, a projector lens is located to expand the beam into the screen. The transmission of the electron beam is highly related to the properties of the material such as density and composition.
3.1.2 Dektak surface profilometer

The Dektak surface profilometer is an instrument to measure the vertical profile of samples, thin film thickness, and other topographical features. Profilometry is a technique to records the quantifies of roughness on the surface. One stylus is moving vertically in contact with a surface and sweeping laterally across the sample for a specified distance. This device works by surface contact measurement function when a very low force is applied to the surface. The display range of the data is up to 655,000 Å (65.5 μm) with a vertical resolution in a range of few Angstrom. The lateral resolution is limited by the stylus shape.

3.1.3 Laser confocal microscopy

Confocal laser scanning microscopy (CLSM) is a technique to obtain high-resolution optical images with the selectivity of depth. Principally, a laser coupled with an optical microscope provides the possibility to achieve precise Z-axis measured data. The advantages of laser confocal microscopy can be stated as follow:

- Enables magnified observation in the air at normal temperature.
- Does not require pre-processing before observation.
- Possible measurement with a large depth of focus.
- Capable of capturing 3D shapes and displaying high-resolution color images.
- Can also measure the film thickness of transparent objects.
- Can observe and measure the surface of samples with steep angles.
- Does not damage the sample surface since the measurements are non-contact.
- Capable of measure long distances.

The confocal microscopy subtracts the out of focus light to get a clearer image. In a normal reflective microscope, the sample is completely illuminated by the excited light, so that the reflected light comes from the entire sample not only the focus point. This out of focus light reduces the resolution of the background image.
Adding a pinhole combination solves this problem and increases the image accuracy by blocking reflected out of focus light.

3.1.4 Contact angle

The contact angle measurement can provide information about surface energy which is related to the adhesion of surfaces [3]. To do the measurement, one liquid droplet rests on a flat and horizontal solid surface and the angle of liquid/vapor interface with solid interface records by CCD camera [4]. The correct value of the angle geometrically acquires by applying a tangent line from the contact point along the liquid/vapor interface in the droplet profile. Basically, small contact angle is achieved when the drop spreads on the surface and large contact angle when it keeps spherical shape on the surface.

Figure 3.1 shows that a contact angle less than $90^\circ$ indicates that wetting of the surface is appropriate and the liquid will spread over a large area of surface. The contact angle bigger than $90^\circ$ generally means that surface is not good wettable so the fluid will minimize its contact with the surface and form a compact droplet. Normally, contact angles greater than $150^\circ$ is the sign of hydrophobic surfaces when $0^\circ$ contact angle indicates complete wetting.

![Figure 3.1: schematic contact angle](image)

As first described by Thomas Young in 1805, the contact angle of a liquid drop on an ideal solid surface can be defined by the mechanical equilibrium of the drop under the action of three interfacial tensions.

$$\gamma_{LV} \cos \theta_Y = \gamma_{SV} - \gamma_{SL}$$

(3.1)

Where $\gamma_{LV}$, $\gamma_{SV}$, and $\gamma_{SL}$ represent the liquid/vapor, solid/vapor, and solid/liquid...
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interfacial tensions respectively, and $\theta_Y$ is the contact angle is shown in fig 3.2

![Diagram showing interfacial tensions](image)

**Figure 3.2:** The schematic of water on the polymer surface and involving surface tensions

3.1.5 Electro-mechanical stability

The IPMC strip has different performance under drive voltage and this response to an electric field is unique character related to sample properties. The basic setup to measure this electro-mechanical response is consisted of a function generator to apply voltage and frequency in different ranges to the metal electrodes. The applied voltage drives the sample when a detector measures the displacement. The most important point for all fabricated samples is the stability of metal layer under applied few volts of the electric field. This characterization technique proves the applicability of sample in general function as an actuator.

3.2 Materials

Basically, IPMC is an ionomer membrane polymer in composite form consist of metal layers on both sides. Ionomers originally have neutral monomers as a backbone plus ionized unit bonded to their subunits [5]. The ionomer properties are determined by two parameters: mole percentage of ion in polymeric structure and quality of interpolation between ions. The electrical conductivity of ionomers despite the nonpolar polymer backbone and its thermoplastic behavior are unique physical properties of
One of the most famous ionomer in commercial configuration is Nafion. The chemical structure of Nafion is illustrated in fig3.3.

![Nafion Chemical structure](image)

**Figure 3.3:** Nafion Chemical structure

This structure is consisted of tetrafluoroethylene group (-CF<sub>2</sub>-CF<sub>2</sub>-)n and the acid group attached to the polymer matrix in the synthesis process. Sulfonic Acid is an organic compound containing the functional group SO<sub>2</sub>OH. The S is a sulfur atom, bonded to three oxygen atoms “O”, one of the oxygen has bonded to a hydrogen atom “H”. The hydrogen can be replaced by a cation such as Na or Mg within hydration process.

The tetrafluoroethylene group with Teflon properties is resisted to chemical reaction, then the ion can move easily in membrane [6]. This combination is the base of multi-functional ionic polymeric metal composite suitable for wide range of application.

The fig 3.4 illustrates polymer structure before and after ionic liquid absorption. The swelling behavior and ion exchange properties depend on the microstructure in the polymer backbone. The swelling ratio is the ratio between membrane weight in the vacuum and the weight after ionic liquid absorption at room temperature. Then different commercial ionomers have distinct swelling ratio result to various properties.

In this work, the polymer was purchased from DuPont Nafion® 117 as a sheet with following properties:

1. The polymer thickness is limited to available product of commercial supplier. The
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Figure 3.4: Polymer structure is swelled by ionic liquid absorption

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalent weight</td>
<td>1100 g/mol</td>
</tr>
<tr>
<td>Thickness</td>
<td>200 µm</td>
</tr>
<tr>
<td>Conductivity</td>
<td>0.1-0.12 S. cm$^2$</td>
</tr>
<tr>
<td>Area resistance</td>
<td>5 Ω . cm$^2$</td>
</tr>
<tr>
<td>Swelling ratio</td>
<td>up to 30% at room temperature</td>
</tr>
<tr>
<td>Volume expansion on hydration</td>
<td>12 – 15%</td>
</tr>
</tbody>
</table>

Table 3.1: Properties of Nafion117

The thickness of polymer determines the volume of clusters and the ion mobility. The thicker sample has better ion mobility but in return, they are heavy and need more force to move. The membrane type Nafion117 with thickness 0.183 mm is chosen to achieve a good balance between sample weight and bending force.

The Nafion polymer turns to IPMC by metalization process on both surfaces. Metal-polymer lamination has a wide range of application as it has polymer properties like light weight and flexibility in addition metal properties like conductivity. Numerous methods are used to improve the adhesion between the polymer and the metal which is not naturally so good. One of a well-established method is chemical reduction processes which used at the beginning of this work [7].

The following materials are required for chemical reduction process:

**Aqueous solution of platinum ammine complex:** Tetraammineplatinum chloride hydrate$[Pt(NH_3)_4]Cl_2.H_2O$, Sigma-Aldrich co.

**Reducing agent for primary reduction:** Sodium borohydride$NaBH_4$, Sigma-Aldrich co.
Reducing agents for secondary reduction: Hydrazine hydrate $NH_2NH_2H_2O$, Sigma-Aldrich co.
Hydroxylamine hydrochloride, $NH_2OH.HCl$, Sigma-Aldrich co.
Ammonium hydroxide solution $NH_4OH$, Sigma-Aldrich Co.
Hydrochloric acid fuming 37%, Carl Roth.
Deionized water.
Sodium chloride.

3.3 Fabrication methods

In this section various manufacturing methods to convert ionic polymer to IPMC will explain. There are two basic methods by using chemical reduction and physical metal deposition. As mentioned before, the Nafion is type of Teflon polymer with a low tendency to adhesion to other surfaces. Moreover for actuation mechanism existence of electric field inside the polymer layer is essential. It has been shown that metal particles penetrated in the polymer can increase effective electric field inside the polymer. Additionally, actuating behaviors of IPMC is strongly depended on the interfacial area between the electrode and the electrolyte.

Then metal adhesion on polymer and particle penetration in polymer interface are two parameters should be considered for all fabrication techniques.

The quality of metalization process on polymer has a significant role on the overall performance of sample by affecting the conductivity of surface electrode and polymer-metal interlocking morphology. The high electronic conductivity through the surface guarantees constant electric field between two electrodes and consequently equal applied force along the sample strip. On the other hand, the large interfacial area between metal particles and Nafion directly improves capacitance of the IPMC. This improvement leads to larger charge accumulation at the electrode layer and consequently better actuation. Besides, the penetrated particles increase the surface area and the intermolecular interaction forces which cause the better adhesion of polymer - metal interface.
3.3.1 Chemical reduction

The chemical reduction to fabricate the IPMC is a multi-steps process to reduce the metal in desired thickness on the polymer surface. This method is a time-consuming process with low possibility to control the parameters at each step. Therefore morphologies of metal layers are significantly different from sample to sample. However, the slow reduction process, allows the platinum to diffuse through the membrane and causes layer by layer metal deposition with stable interpolation. The whole preparation steps are depicted in Fig 3.5 and explained in detail afterward.

The fabrication process consists of three main steps, conditioning, coating and immersing [8]. The several physical and chemical processes are included in each step. The whole procedure has high sensitivity to the temperature condition and velocity of reaction.

All steps are explained in below:

**Conditioning**

- Polymer preparation: The polymer film was cut into the size of 6.5cm×3cm (Resulting surface area 19.5 cm² per sample). The total amount of material for the chemical process must be calculated based on the surface area of the sample at both sides and multiply by the number of samples.

- Plasma treatment: The polymer membrane has a low surface energy and poor wet ability. Then to improve the coating adhesion the surface of the membrane was cleaned by plasma. This treatment was carried out by Diener Electronic Femto on both polymer sides for 5 minutes at power 100 watt.

- Cleaning: Impurities and ions inside the membrane must be removed before coating by hydrochloric acid. The membrane was boiled in HCL 2 N for 45 minutes at 75 °C.

- Washing: Hydrochloride dusts from the reaction of hydrochloric acid with polymer must be removed. The sample was boiled in deionized water for 45 minutes at 75 °C also the sample can be stored in water before next steps.

**Coating**

- Soaking in Pt salt solution: For chemical coating of platinum on Nafion, the mem-
Figure 3.5: Chemical fabrication steps for IPMC
brane should be immersed in a platinum complex solution, tetraamine platinum(II) chloride monohydrate ([Pt(NH$_3$)$_4$]Cl$_2$H$_2$O), for several hours. The amount of Pt salt for aqueous solution estimate base on the surface area of a sample when the desired Pt concentration is more than 3 mg/cm$^2$. To neutralize the solution 0.5 ml ammonium hydroxide (NH$_4$OH) is added to above solution. When the cleaned membrane is immersed in an aqueous solution of platinum, based on equation 2.7 and 2.12, the cluster structures are formed by uptaking water. The cation complexes diffuse into the membrane to replace the protons inside the polymer component.

- Primary plating: At this step, reducing agent sodium borohydride (NaBH$_4$) was used to reduce the Pt particle inside the surface and coats the metal at inner surface of the polymer. To obtain the total reaction from metal salt aqueous solution till coated Pt particle formula 3.1 is given:

$$NaBH_4 + 8OH^- \rightleftharpoons BO_2^- + Na^+ + 6H_2O + 8e^-$$

$$4[Pt(NH_3)_4]^{2+} + 8e^- \rightleftharpoons 4Pt + 16NH_3$$

$$4[Pt(NH_3)_4]^{2+} + NaBH_4 + 8OH^- \rightleftharpoons NaBO_2 + 6H_2O + 4Pt + 16NH_3$$ \hspace{1cm} (3.2)

Based on equation 3.2, the reducing agent contains anion, therefore, it does not migrate into the membrane. According to dipole density from equation 2.10, the platinum ammine complex diffuses towards the outside of the membrane. Then just at the surface region the platinum salt is reduced by reducing agent and the metal layer can only takes place on the membrane surface especially in distance few micrometer near the surface. The solution was heated step by step from 40 °C to 60 °C in 2 hours and kept at 60° C for 1.5 hours to help diffusion acceleration and improve the output.

Sodium borohydride is a very strong reducing agent; this can be observed easily if a small amount of NaBH$_4$ is applied to an aqueous solution of platinum salt. The solution turns to black instantly when the solution heated up. In this fast chemical reaction, to avoid the possibility of hydrogen gas formation and the danger of an explosion, sodium borohydride should never be applied to a hot solution directly.
Always it should be added to cold solutions and start heating afterward. This step which called primary plating can be repeated as much as needed to increase the metal amount penetrated into the polymer. Principally the shape of penetrated layer also plays critical role to apply bigger electric field inside the polymer. In ideal case, dendrite shape of penetrated particle could be observed.

Fig 3.6 illustrates transmission electron microscopy (TEM) of Pt penetrated in membrane. Base on other report [9], 1-20 µm is optimum depth to achieve best performance.

- Fixing: After last primary plating, the constructed dendrite shape plus thin metal layer on the surface, need to stabilized. Keeping the sample in diluted hydrochloric acid 0.1 N for one hour is recommended to store and conserve the reduced platinum.

- Secondary plating: High quality IPMC sample must have great conductivity on surface electrodes. This plating step is a reduction process to make more metal layer on primary layer and increases the electrode thickness. The reducing agents for secondary plating are Hydrazine($N_2H_4$) and Hydroxylamine($NH_2OH$) that both of them have week reducing power compared to sodium borohydride. In this step, it is necessary to reduce the platinum slowly on primary metal layer to achieve several metal layers. The first coated layer, prevent the sample to absorb platinum-ions during immersion. Hence, for the secondary plating the reducing process has done in platinum-salt solution and sample dos not need to immerse before the reduction process. Then diluted hydrazine hydrate and hydroxylamine hydrochloride are ap-
plied to a platinum-salt solution bit by bit when the temperature goes up slowly. This step also, can be repeated to reach maximum electrode thickness. The fixation step provides stable sample by help of diluted hydrochloric acid in final secondary plating.

Chemical reduction process for hydrazine hydrate is explained in equation 3.3.

\[
2N_2H_4 \rightleftharpoons N_2 + 2NH^+_4 + 2e^-
\]

\[
2[Pt(NH_3)_4]^{+2} + 4e^- \rightleftharpoons 2Pt + 8NH_3
\]

\[
4N_2H_4 + 2[Pt(NH_3)_4]^{+2} \rightleftharpoons 2N_2 + 4NH^+_4 + 2Pt + 8NH_3 \quad (3.3)
\]

And for hydroxylamine hydrochloride is explained in equation 3.4.

\[
NH_2OH + 2H_2O \rightleftharpoons NO_3^- + 7H^+ + 6e^-
\]

\[
2[Pt(NH_3)_4]^{+2} + 4e^- \rightleftharpoons 2Pt + 8NH_3
\]

\[
6[Pt(NH_3)_4]^{+2} + 2NH_2OH + 4H_2O \rightleftharpoons 6Pt + 24NH_3 + 2NO_3^- + 14H^+ \quad (3.4)
\]

The secondary plating or repetition of this step should do gradually to avoid bulk construction in the metal electrode which destroys the chance of creating cracks on coated layer. The cracks are essential for the ionic liquid transition which is the main reason of osmotic pressure and bending.

The chemical reduction as a common method for IPMC fabrication is a procedure with low efficiency and several main drawbacks. In this method, electrode forms step by step under fabrication condition when the quality of coated electrode is very sensitive to the condition. That means any changing on setting circumstance can affect the morphology of final products. Thus the sample function depends on lots of important details and the following points improve reproducibility of chemical fabrication. The solution concentration must be precisely calculated and the temperature must be controlled exactly to tune the reduction speed and the membrane should exposes to influence of reducing agent in a stable setup. To avoid
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wrinkling or bending of polymer during the process the sample should remains flat as much as possible otherwise the homogeneous metalization can not achieve then, the sample was fixed during the chemical process by a Teflon holder shows in fig3.7. Also a blender should rotates in solution during reduction which can accelerates exit of produced gas from reactive area.

![Teflon holder fixes the sample during the reduction process](image)

**Figure 3.7:** Teflon holder fixes the sample during the reduction process

The quality of final products by mentioned process is controlled by electron microscopy. The surface of the metal electrode after chemical reduction is shown in fig 3.8a. The existence of crack is clear in the image which these cracks help ions transfer from solution toward Nafion membrane.

The SEM also can be used to get a cross section view of the membrane. In figure 3.8b the arrangement of two metallic layer and thick Nafion membrane are observable. The cross-section image shows clearly nonuniform layers on both sides as a result of the chemical reduction.

In transmission electron microscopy, as the density of metal and polymer are different, the penetrated platinum particles into the polymer surface are detectable in the background of Nafion (figure 3.8c).

For all the SEM measurement a Hitachi S-5200 and for TEM measurements the model JEM-1400 Plus from JEOL ultimate in 120 kV were employed.

In summary, IPMC sample can be fabricated in multiple chemical steps. The good adhesion between polymer-metal and penetration of metal inside the polymer, which both of them improve the IPMC performance, are advantages of this method. There are also some disadvantages regarding chemical method. The hazardous chemicals are involved in chemical reduction. Also this method has limitation on the possibility
Figure 3.8: Electron microscopy (a) SEM (b) SEM, cross section (c) TEM, cross section
to control the process for thickness and coated area. Additionally, by chemical method the final homogeneous sample comes out from the center part of the original sample after cutting the edges. This fact limits miniaturizing of IPMC to small size. To improve the quality of final products and avoid of chemical procedure, physical methods to coat the metal on the polymer is a good alternative. These methods will explain in next section.

3.3.2 Physical method

As mentioned in the previous section, chemical metalization needs multi steps process. Also it is hardly possible to adjust the thickness of the metal layer and also the depth of penetration for the metal particle in the polymer. To gain more control in metalization process, a physical deposition method can be useful.

Metal-polymer laminates can be achieved by various processes like physical vapor deposition (PVD), hot press or sputtering. They all have a wide range of applications as they have the possibility to prepare samples in every desired size. One of the critical parameter in all mentioned process is adhesion between polymer and metal layer which is not mostly strong enough. In a case of IPMC the penetrated metal particle also is a critical parameter, and then these two main challenges should be considered by physical method. The metal penetration problem can be overcomed by Nafion surface patterning to make holes on the surface. These holes let metal deposit inside the polymer layer which simulate the metal penetration by chemical reduction. To improve the metal-polymer adhesion, surface treatment as a normal solution has been tested by different techniques.

As Nafion is a type of Teflon and has high resist to deformation, then surface patterning must be done with specific consideration [10]. In our work, two different approaches are followed to make hole patterns on the polymer surface. In the first approach, a spiky mask has been used as a stamp on Nafion by a hard press and in the second one, electro-beam etching makes the desired shape on the polymer.

**Structure stamp:**

The patterns on Nafion should have micrometer depth to produce a comparable...
penetration to chemical reduction after metal deposition (fig 3.4). To make this shape on the polymer, an array of SU-8 pillars was used as a stamp to press the polymer at high temperature.

SU-8 is a photoresist epoxy was designed after 1980 instead of a silicon wafer to fabricate a high-resolution microstructure mask. The SU-8 is a negative photoresist which reacts differently from positive photoresist [11]. For positive resists, the UV light can change the chemical structure of the resist so that it becomes more soluble in the developer. But the negative resists like SU-8 behave in the opposite manner. Under UV exposure, negative resists polymerize and make it resistant to dissolve. Therefore, the negative resist remains on the surface wherever it is exposed. The SU-8 is sensitive to UV (350-400) nm then Under UV light, the chemical process occurs and makes a thermally and chemically stable structure.

The ultra-thick microstructure can be fabricated in following sequences: substrate treatment, spin coat, softback, expose, post expose bake (PEB) and develop. The most important step is spin coating when the best outcome is highly uniform surface without any edge bead effect. This is possible by SU-8 when it is self-planarized under spin coater. Additionally, to coat a film with a millimeter thickness in just one step, the viscosity is a critical parameter. The SU-8 has a low molecular weight which allows using high concentrations during spin coating. These two properties suited SU-8 for ultra-thick applications and provide final pillars with height diameter from 1 to 500 micrometer.

The prepared SU-8 stamp has 10 (µm) pillars height. The trace of this stamp after pressing on polymer surface should provides the regular pattern on desired depth. The final micropillars are shown in fig 3.9.

As mentioned before, the Nafion resists against deformation, then the stamp must apply on the surface under pressure at high temperature. The SU-8 pillars are quite hard and stable then the polymer can sandwich between two SU-8 plates under pressure at 100°C for 12 hours. After that, it needs enough time to reach to the room temperature which is a right time to separate stamp from polymer surface.

The created hole structures on polymer surface are measured by Dektak profilometer and the results come in fig (3-10 a) for front sides of polymer and fig (3-10 b) for the back side.
Contact profilometry shows, the hole structures on Nafion surface are created but not uniformly in all parts of the surface. Additionally, the depth profile of them is around 200 nm which is much smaller than the pillars size. This mismatch is a sign of not perfect contact between the stamp and the membrane during the process. The results prove of possibility to have pattern on both sides of Nafion but clearly, the structures are not uniform along the sample even in micrometer distance. The non-similarity on the pattern when the similar stamps with equal height are used comes from wrinkling of the polymer under pressure or temperature shock. The existence of a not flat surface is proved by the wave shape in profile image. The inhomogeneous pattern is not able to provide a sample with high quality, then using SU-8 stamp is not a practical way to pattern the Nafion.

On the other hand, stamp peel off process sometimes leads to the broken pillars and fragmentary part of SU-8 can be found in the pattern. The main aim of patterning on the polymer is to gain unfilled holes on the surface which are ready for vapor deposition. Then, the defective peel off reduces the efficiency of the method. Due to problems in stamping method, we examine other techniques to make more effective hole structures.

**Electro beam etching:**

The position, thickness and geometry of electrodes have an essential role on IPMC performance. Therefore we investigated the micropatterning on polymer by direct
Figure 3.10: Dektak profilometer of stamped polymer (a) front sides (b) back sides
Electron Beam Lithography is a commercial technique to create accurate patterns in micro and nano size. To achieved arbitrary two-dimensional patterns, the polymer surface covers by resist layer then the focused electron beam changes the chemical properties of exposes area. Afterwards, the undesired parts can be removed by a proper solvent. The shape and size of pattern cab be controlled by E-beam power and expose time.

Electro beam etching is a flexible technique by a variety of parameters for precisely control the shape and depth of final structure. In a case of Nafion polymer, it is critical to find an appropriate parameter to make the stable cavity shape in the regular distance. Fig 3.11 simply shows the preliminary result to make separate holes on Nafion with an electron beam.

To control the stability of structure in continues length; several parallel lines are written on the substrate at different power and expose time. Figure 3.12 corroborates electron-beam lithography potency to extend unbroken lines over 10 mm. The results are repeatable with equal quality which makes this method of patterning a practical method.

The suitable exposing power, ensure stable pattern on a surface without damaging the polymers. The series of study have been done to find out the suitable current of focused electron in the lithography process. Two extreme examples of results show
that at current below 200 $\mu$C/cm$^2$ (too low intensity) the shapes are not dominant and under current above 700 $\mu$C/cm$^2$ (too high intensity) destruction of material is clear in fig 3.13.

Figure 3.12: Parallel lines on polymer fabricated by E-beam

Figure 3.13: The effect of E-beam intensity on pattern (left:too low intensity)(right:too high intensity)

Then the parallel lines with desired depth can be created by E - beam. The next step is to make regular holes structures on both sides of the polymer. These holes are the place which will be filled by metal deposition and can play a role similar to penetrated particles in chemical fabrication method.

To compare different patterns on the polymer by electron beam etching, laser confocal microscope is used. In this research KEYENCE’s VK-9700 3D laser scanning microscope is employed while the laser light passes through the X-Y scanning optical
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system and across the sample surface. The photomultiplier detects reflected light only for positions in focus by the confocal optical system. A fully focused image is created by accumulating in-focus position information in the Z-axis direction. At the same time, the focal position of the objective lens record to measure the 3D shape of the surface. Fig 3.14 shows a structure with desired hole pattern on Nafion polymer.

Based on laser microscopy results, sample has holes structure at a depth of few micrometer which is appropriate penetration distance. The results prove the potential of the method to print every demanded structure in very regular forms. In our work, the pattern includes circular and linear structures but the technique is not restricted to these shapes. By using Klayout program which is Smart drawing function with many options, there is no limitation on pattern shape and density.

The stability of pattern was tested after soaking the sample in ionic liquid. The swelling of the polymer after water uptake detach the metal layer in most part of polymer which is observable in (fig 3.15). According to the result, weak adhesion

Figure 3.14: E-beam pattern on polymer surface
between metal and polymer limit the usability of the physical method for IPMC fabrication. Hence the adhesion should be improved. Different surface treatments for adhesion improvement were used and the effect was studied by contact angle measurement that will explain in next part.

Contact angle

Surface roughness is one of the important factors which can influence the mechanical properties of the two surfaces. There are several reports on the improvement of the bonding strength due to roughness increment [13]. On way to increase roughness is to bombard the surface with plasma ions. The first plasma treatment has done by Diener Electronic Femto device which works with atmospheric plasma at 100 W for 5 minutes. The second treatment has done by Veeco ion beam etching device work with Argon at 50 W for 5 minutes. To verify the result of these two treatments, contact angle measurement was used.

For contact angle measurement, a commercial device, Dataphysics OCA 15 with SCA 20 software was used. This device has an automated syringe which the injection
value and speed of liquid flow were controlled with a motor. A 10 µL water drop with speed of 1 µL/s was placed on the surface of the polymer. The image of a stucked drop was captured with a CCD camera while water drop was illuminated from the back side. The setup image with detail is shown in fig 3.16.

To achieve reliable value, measurement had repeated several times for each point and it had done on different points of the substrate.

![Contact angle measurement device](image)

**Figure 3.16:** Contact angle measurement device

To consider the effect of plasma on polymeric roughness, two basic group of samples are prepared. The first one was treated with atmospheric plasma and the second one was treated by argon plasma etching. Also, a sample without any treatment is used as the reference. The stability of the treatments has been tested after 1 and 24 hours by contact angle measurement again.

Results for reference polymer and two treated samples have been shown in fig 3.17. figure a-c represent the contact angle of the reference sample and atmospheric and argon etched one. The results in figures (d) and (e) measured after one hour and figure f and g after 24 hours. The reference sample contact angle remains constant during the time so it just has been showed one time.

The average contact angle values for all measurements are shown in table 3.2 when
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Figure 3.17: Surface treatment effect
all measurements repeated for 5 different points of each sample.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>First contact angle</th>
<th>Angle after one hour</th>
<th>Angle after 24 hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion</td>
<td>106.3</td>
<td>105.9</td>
<td>105.6</td>
</tr>
<tr>
<td>Nafion + plasma</td>
<td>75.2</td>
<td>92.5</td>
<td>93.9</td>
</tr>
<tr>
<td>Nafion + Argon</td>
<td>89.0</td>
<td>86.7</td>
<td>84.5</td>
</tr>
</tbody>
</table>

Table 3.2: Contact angle

Base on the result, the effect of atmospheric plasma on roughness for Nafion, is not stable enough to keep the effect until metal deposition after treatment. But Argon etching is able to treat the substrate in appropriate condition for a longer time. Then this treatment is a good candidate to improve adhesion of polymer before metal coating.

For further progress, one argon etched sample and one not treated sample were coated with Platinum by thermal evaporation deposition in 5 nm thickness. Then both samples were bombarded by electron beam in a SEM device.

Based on the figure 3.18, for the non-treated sample metal surface has been fragmented under electron shoot while the argon etched one mostly keep continues structure until it totally destroyed. We conclude that the roughness increment can effect the metal-polymer adhesion and keep continues structure under influence of E-beam.

### 3.3.3 Metal deposition

In previous sections, it was shown that E-beam technique is successful to write arbitrary pattern in ordered shape with control on depth and density of pores. Afterward, the argon etching was used to improve the adhesion between metal and polymer in which the results prove the stable effect of this treatment. Now we will explain thermal evaporation and sputtering methods to deposit the metal layer on a patterned polymer. A series of samples prepared to find out the efficiency of each method and check the maximum possible metal thickness which is stable in ionic liquid and under actuating voltage.
Figure 3.18: Metal layer stability under electron beam bombardment (a) Metal coated on Nafion (b) Metal coated on argon etched Nafion
**Thermal evaporation:**

Thermal evaporation is a common method to deposit metal films. Metal heats up to the point of vaporization and then evaporates to form a thin film covering the surface of the substrate. All film deposition takes place under vacuum to make a pure uniform layer in all parts of the sample. To clean the samples before deposition, they immerse in 2 M HCl at 75 °C for 45 min and subsequently rinse in deionized water.

For all samples, Nafion was patterned by E-beam and then was treated by argon etching. Afterward, different metals have deposited on the samples as follows:

\[ P_1 : 100 \text{ nm Aluminum} \]

\[ P_2 : 5 \text{ nm Titanium, 50 nm Gold, 5 nm Titanium, 50 nm Aluminum.} \]

The Titanium layers exert between layers to increase the adhesion. Both samples swell in NaCl 0.9% as an ionic liquid.

**Sputtering:**

Sputter deposition is a physical method to deposit conductive materials by ejecting metal from a target on the substrate. Here, all used samples are patterned and treated by argon. The process starts with sputtering of 20 nm Gold and then continues further by 20 nm Platinum sputtering and repetition of platinum deposition to achieve final thickness 100 nm electrode.

The sample prepared by sputtering is called \( P_3 \) and immerse in ionic solution (NaCl 0.9%) after sputtering.

To clarify the ability of the physical method to make IPMC, the samples \( P_1 \), \( P_2 \) and \( P_3 \) were analyzed by electromechanical measurement comes in next section.

**Electro-mechanical stability**

In our work, the function generator was HAMEG HM 8130. It can be used for the output of rectangular or sinusoidal form with the possibility to adjust amplitude and frequency.

The detector was typical laser displacement which can be calibrated to different distance ranges related to different sensitivity. The device was Welotec OWLF 4030 FA S1 with an output range from 0-10 volts to cover a wide range of displacement.
The strip holder was made from a Teflon clamp with gold electrodes to apply electric field directly on the sample. More details about electromechanical characterization on samples from chemical reduction comes in chapter 4. This section concentrates just on three samples as products of physical fabrication.

**Sample** $P_1$: The metal layer of sample $P_1$ is stable in ionic solution but it separates from polymer by applying voltage.

**Sample** $P_2$: The sample $P_2$ acuates under applied voltage until 1 volt but by further increasing the voltage, metal separates from surface which is shown in figure 3.19a.

**Sample** $P_3$: For the final sample $P_3$ prepared by sputtering, specimen demonstrates stability of the metal layers by immersion in ionic solution and under applied drive voltage (3.19b) while short actuate is obvious in electro-mechanical measurement.

As sample $P_1$ and $P_2$ are stable in ionic solution but not under voltage, it can be concluded the surface treatment is not enough to bond polymer-metal in dynamic acuating case. Then the surface treatment just makes a weak adhesion to keep metal layer on the surface in a static case (in swelling state) in ionic solution.

In comparison to metal evaporation, sputtering after surface treatment provides stronger adhesion between metal and polymer. The acuating of sample $P_3$ is compared with chemical fabricated samples in chapter 4 (table 4.2).
Figure 3.19: Metal layer on patterned polymer after applying voltage (a) vapor deposition (b) sputtering
Bibliography


Chapter 4

Actuator properties

Electroactivity properties of polymeric material can be demonstrated by motion or extension of the polymer under applied bias voltage. The previous chapter clarifies the polymer metallization of a swollen membrane laminated between two metal electrodes to make IPMC sample. They can be used as electromechanical and mechanoelectrical transducers. In case of the electromechanical transduction, electrical energy converts into motion, whereas in a case of the mechanoelectrical transduction, mechanical movement converts into electrical energy (it can be measured as voltage or current) [1]. Then IPMC has actuator and sensor functions separately.

In addition to single actuating or sensing function, IPMC can exhibit both functions simultaneously to detect its motion which called self-sensing. In chapter 4, mechanism of actuating motion will be explained considering theoretical background from chapter 2. Additionally, the dependency of sample displacement to voltage and frequency is also studied.

The mechanism of interaction between electric field, mobile ions and actuation of IPMC is not well understood but it strongly depends on sample properties. These properties are disparate from sample to sample as a result of variety of fabrication methods and furthermore several complex steps even in similar fabrication method.
4.1 Actuate mechanism

Ionic polymer, in our case Nafion, is porous polymer almost filled with ionic liquid. The polymer is an ion conductive medium under electric field at condition explained in equation 2.12. The clusters are filled by the ions until the total pressure inside is equal to osmotic and electrostatic pressure. An ionic liquid such as NaCl has $Na^+$ ions surrounded by the water molecules, which they can freely move in the polymeric membrane after replacement in the polymeric structure. Plated metal electrodes on polymer surface connected to AC voltage provide an electric field between anode and cathode. Mobile cations inside the membrane migrate towards anode due to an applied electric field and carry water molecule bonded to them. The water volume is changed in anode area and causes expansion of the material at one end. Chemical potential variation happens as a result of this concentration alteration according to equation 2.19. Equation 2.18 illustrates ion flux in consequence of electric potential and chemical potential interaction.

Based on equation 2.24, the rate of changes for water in membrane cause force on sample and bend it toward the anode and the subsequent relaxation in the opposite direction. Back relaxation occurs soon after actuation while cations are migrating back into the cathode side and carrying with them the water molecules.

![Figure 4.1: Bending mechanism](image)

According to references, the IPMC actuation mechanism can be explained by several models [2]. A primary model suggested that combination of water pressure
Actuator properties

gradients and the overall electric field as thermodynamic forces cause ion/water fluxes and movement. Others suggest an electromechanical model when water flow, induced by pressure gradients and electro-osmotic flow, swell the area near the electrode and drive the sample. The fulfill model conclude that the electrostatic and osmotic forces in the polymer microchannels generate the actuation. In this model, the osmosis force controls water flow in or out of membrane and is responsible for back relaxation movement after actuation. This concept is able to explain actuation and sensing behavior of IPMC in a clear way.

To characterize the electro-mechanical response of an IPMC, tip displacement has been measured by a laser distance sensor. The component and mechanism of this measurement by the laser is described in next section.

4.2 Laser displacement sensor

Base on the situation, there are several techniques to measure displacement or distance. The most important factor for choosing a suitable sensor is the measurement range and required accuracy for the evaluation. Additionally, the arrangement of the objects to be measured is also determinative to find the best method. For linear distances of a few centimeters with high accuracy requirement, triangulation sensor is the common technique. In this method, the laser beam is reflected from an object surface back to an array of photodiodes (PDA) located at the laser position. The detector measures the variety of angle from two known points at either end of a fixed baseline and whole processes determine the distance.

The laser distance sensor Welotec OWLF 4030 FA S1 is used in this work. To use this sensor method, the device must set to certain distance related to voltage base on required measure range and necessary resolution. Technical detail of our sensor shows that possible measuring range is maximum 100 mm with micrometer resolution when the output voltage is in range 0-10 volts.

The first selected position aligns with 0 V and the second position aligns with 10 V when the distance between these two points can be divided to 10 volts. The function is shown in fig 4.2 and technical details are determined by table 4.1.
Actuator properties

Figure 4.2: Laser displacement function

<table>
<thead>
<tr>
<th>Detail</th>
<th>4030 FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measuring range</td>
<td>50 - 300 mm</td>
</tr>
<tr>
<td>Min step range</td>
<td>less than 5 mm</td>
</tr>
<tr>
<td>Resolution</td>
<td>10 - 330 µm</td>
</tr>
<tr>
<td>Voltage output</td>
<td>0 - 10 V</td>
</tr>
<tr>
<td>Current output</td>
<td>4 - 20 mA</td>
</tr>
<tr>
<td>Power supply</td>
<td>12 - 28 V DC</td>
</tr>
</tbody>
</table>

Table 4.1: Laser displacement properties
4.2.1 Laser calibration

For laser displacement measurement, the distance of one object is calculated by the angle of reflected beam while a built-in microcontroller converts these nonlinear relations between distance and angle to the output signal in the form of voltage which is related to the distance linearly. The function of this method depends strongly on the medium which the laser beam runs and the evaluation condition. Therefore the dependency of distance to voltage should calibrate before real measurement.

To achieve exact displacement value in the measurement condition, the laser sensor adjusts to the front side of sample strip while the strip is held by the clamp vertically. The calibration procedure is shown in 4.3 in a way that tip moves with step motor while the voltage related to displacement records step by step. The laser should be calibrated for each target medium separately. For example, if final measurement should run in water, calibration should be also done in water or a solution with similar reflection index.

![Laser displacement calibration](image)

**Figure 4.3:** Laser displacement calibration

This calibration evaluation was repeated several times and mean values of all
measurements were plotted for displacement versus voltage. The plot with fitted line shows in fig 4.4.

\[ D = -1.51(mm/V)V + 26.09(mm) \]  \hspace{1cm} (4.1)

According to the plot, by simple interpolations, displacement and voltage output obviously have linear relation. The minimum measurable voltage is 0.059 V at a distance of 26.09 mm, and the maximum value is 9.33 V at a distance of 11.33 mm. By using linear regression measured displacement D in mm versus voltage in volt can be calculated as:

\[ D = -1.51(mm/V)V + 26.09(mm) \]  \hspace{1cm} (4.1)
4.2.2 Curvature

Along with sample displacement, the size of strip is also important to keep the standard for sample performance comparison. Hence, it is necessary to convert the displacement values into a parameter which is not depended on sample length which is known as curvature.

\[ R = \frac{L^2 + D^2}{2D} \]  

Figure 4.5: Displacement-curvature

The curvature value is calculated by the following equation considering sample length (L) and horizontal displacement (D):

After laser calibration, all measured voltage by laser sensor can be converted to the horizontal displacement. Then by using equation 4.2, the curvature of each sample can be calculated which is a standard indicator to show the response of each sample to electric field.

4.3 Electro mechanical displacement

Mechanical response of IPMC strip to electrical stimulation measures by laser sensor in an optical system, then this method nominates as optoelectromechanical setup.
Actuator properties

The schematic experimental setup in fig 4.6 shows IPMC sample hangs up in the air by dual electrode hanger. The drive voltage at the different frequencies and amplitudes apply on the electrodes. Then the displacement value measures by laser sensor which transfers data to Labview software that can records it as voltage.

Figure 4.6: Electro mechanical displacement experimental setup

4.3.1 LabVIEW Program – multichannel scope

The dynamic reaction of IPMC under AC electric signal is measured as a voltage and transferred as input data to NI USB 6008 interface which is connected to software LabVIEW.

LabVIEW (Laboratory Virtual Instrument Engineering Workbench), created by National Instruments is a graphical programming language that uses icons instead of commands to create the function to be used for Data acquisition, signal Processing, and hardware control. This program generally can be modified for lots of application
by determining the input parameters as desired physical parameters for measurement from voltage to current or temperature and more. In our case, multi-virtual channels, named as Dev1/ai1, Dev1/ai2, Dev1/ai4 and Dev1/ai6, are defined in series to measure voltage through the connection points.

The LabVIEW program generally is consisted of front panel window and block diagram window. The front panel is a place for indicators and control element (input and output display). The minimum and maximum recordable values can be defined by the user at front panel as well. The sample rate and also sample rate per channel can be adjusted in front panel diagram for each measurement.

![Labview front diagram](image)

**Figure 4.7:** Labview front diagram

Block diagram is corresponded to the front panel by constants parameters, functions, SubVIs, structure and wires that connect data from one object to another. The basic codes are also located in block diagram. The number of channels can be changed by activating different subprogram in block diagram from 2 channel to 4 channel and from 10000 sample rate per channel to 5000 in a case of need. Block and front diagrams are shown in 4.11 and 4.12.
Actuator properties

Figure 4.8: Labview block diagram
4.3.2 Electro mechanical results

The electro mechanical behavior of fabricated sample in chapter 3, are analyzed in this section. Six different samples $S_1$ to $S_6$ are fabricated by chemical reduction and one sample $P_3$ by physical method comprise of e-beam patterning and sputtering metal deposition are characterized by above mentioned system at frequency 0.25 and voltage 3 volt.

The actuating of all samples are tested and results based on sample properties and curvature value are presented in table 4.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Characteristic</th>
<th>Curvature+Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>Primary plating</td>
<td>2(mm)+0.3</td>
</tr>
<tr>
<td>$S_2$</td>
<td>Primary plating + secondary plating</td>
<td>8.5(mm)+0.1</td>
</tr>
<tr>
<td>$S_3$</td>
<td>Primary plating + 2secondary plating</td>
<td>15.3(mm)+0.2</td>
</tr>
<tr>
<td>$S_4$</td>
<td>Primary plating + 3secondary plating</td>
<td>21.8(mm)+0.1</td>
</tr>
<tr>
<td>$S_5$</td>
<td>2Primary plating + 3secondary plating</td>
<td>23.1(mm)+0.0</td>
</tr>
<tr>
<td>$S_6$</td>
<td>3Primary plating + 3secondary plating</td>
<td>24.6(mm)+0.0</td>
</tr>
<tr>
<td>$P_3$</td>
<td>Physical plating</td>
<td>0.4 (mm)</td>
</tr>
</tbody>
</table>

Table 4.2: Samples properties

According to the curvature value, secondary plating and its repetition can effectively increase the bending while duplication of primary plating does not have the same magnitude of effect [3]. The function of sample $P_3$ prepared by the physical method, is not acceptable yet and need improvement to increase the electrode thickness which is possible by galvanization process, explained in 3.3.3.

Further measurements have been done on IPMC to examine sample response at various frequency and voltage amplitude. For this series of test, sample $S_4$ have been chosen while it has proper curvature. For all measurements IPMC strip hangs in the air by dual electrodes hanger which has been designed for the set up to apply the electric field in a stable sample position through a two metal plates attached on a clamp.

Fig 4.9 shows the Teflon sample holder with gold electrode which design for this measurement. The shape of sample holder and amount of pressure it might apply on
sample has effect on function [4]. Then, using stable and suitable holder is critical to achieve the results in similar condition.

![Figure 4.9: Teflon holder](image)

### 4.3.3 Frequency dependency

This section considers the effect of frequency variation on IPMC performance while the sample strip runs under drive signal at the constant amplitude. The frequency alters in the range of 0.25 Hz to 2 Hz. The measurement repeats three times for amplitude of 2 volts, 2.5 volts and 3 volts while horizontal movement values record by laser displacement. The results are plotted in fig 4.10 which shows, IPMC sample has a better function at the lower frequency which is related to the response time of ions to applied electric field. At lower frequency, ions have enough time to move across the polymer membrane and force the water molecule to flow in microchannel. More osmotic pressure clearly means more bending. As the frequency increases, the ions cannot follow the frequency and finally in a specific frequency, ions become completely immobile[5].

As mentioned before, the lower frequency corresponds to higher displacement. When frequency goes to zero, the AC signal converts to DC signal and sample has the highest displacement. The disadvantage of using DC signal is that due to back relaxation of ions, the sample gradually comes back to initial position. Hence to avoid this problem and also depend on the application, the AC signal with low frequency mostly is used to drive IPMC.
Figure 4.10: Displacement versus frequency dependency
4.3.4 Voltage dependency

IPMC sample performance depends on not only the frequency but also the amplitude of applied voltage. When the drive signal is not strong enough to move the ions effectively, there is no water flow to cause the bending. By increasing the amplitude over 1 volt, physical bending is detectable and by more raising the voltage bigger displacement occurs. The top amplitude limitation is where applied electric field ionized the water molecule and cause gas bubble which disturbs the soft and normal actuation. To investigate the effect of voltage amplitude on IPMC function, one measurement runs at the constant frequency when the applied voltage sweeps values from 20 mv to 3.5 v which is the limitation of the driving voltage. The experiment has repeated for three different values in frequencies of 0.25 Hz, 0.5 Hz and 1 Hz.

Fig 4.11 shows the results of laser displacement sensor are recorded for this series of test.

![Figure 4.11: Displacement versus voltage dependency](image)

**Figure 4.11:** Displacement versus voltage dependency
As expected, the higher displacement is observable when voltage amplitude increases. It also showed that more bending happened at measurement by lower frequency [5]. By here, the actuating properties of samples under different voltage and frequency have been investigated. Based on the discussion in section 3.3.3 the thickness of metal electrodes can affect the IPMC function. Then in the next section, metal thickness and circumstance of metal layers coverage will study by measuring sheet resistance.

4.4 Sheet resistance

Chapter 3 explained different fabrication methods to produce the IPMC sample. All methods need to coat metal layers on both sides of polymer which is essential for actuate function. The quality of metal layers have an important role on sample motion. The quality mostly means, surface conductivity to provide effective voltage along the actuator. The metal coverage over the polymer and surface conductivity can be compared by surface resistance measurement from sample to sample. Then surface resistance is a useful parameter to determine the electromechanical response of IPMC and compare the performance [6]. Additionally, for mechanoelectrical behavior and sensor application of IPMC (Chapter 5), we assume that the surface resistance of the sample is comparable to the resistivity of the sample while the thickness of the sample is very small. Based on this assumption, for the new sensing method it is important to find the surface resistance of samples as a thin sheet.

The Van der Pauw method is a technique commonly used to measure the resistivity of a sample in any arbitrary shape when the sample can approximately assume as a two-dimensional bulk for example metal plates on IPMC surfaces. The Van der Pauw method is enable to calculate average resistivity of the sheet by measuring voltage and current at four-point probe placed around the sample in two steps. In this setup, DC current applied to two points when voltmeter measures the voltage between two others as it shows by schematic image in fig 4.12.

By using Van der Pauw technique, the resistance obtains from following equation:
According to equation 4.3 and choosing four electrical contacts in corners from AB to CD we obtain:

\[
R_{\text{vertical}} = \frac{R_{AB\ CD} + R_{CD\ AB}}{2} \quad R_{\text{horizontal}} = \frac{R_{BC\ AD} + R_{AD\ BC}}{2} \quad (4.4)
\]

When

\[
\exp\left(-\frac{\pi R_{\text{vertical}}}{R_s}\right) + \exp\left(-\frac{\pi R_{\text{horizontal}}}{R_s}\right) = 1 \quad (4.5)
\]

The Van der Pauw method is appropriate technique under some conditions: the measured surface should be flat with a uniform thickness without isolated holes [7]. Additionally, the sample should be homogeneous and isotropic while four contact points are at least few order smaller than the sample size. Fig 4.13 shows measurement set up.

As the surface resistance along the length of the sample is really small a very sensitive device is needed to measure it. Another possibility to increase the measured value is applying more current to the sample but it leads to raising the temperature. One should consider the heating effect on sample properties which makes much
error in this procedure. By considering this inaccuracy, some modification in setup have been done to improve the sensitivity and accuracy. For this improvement, the contact points of four probe should be stabilized to reduce errors related to bad contact and unequal force along the points. Figure 4.14 presents new ohmic holder, to have more stable contacts and the uniform force on the sample.

In addition, the thermal effect and error can be avoided by using AC current source instead of DC and amplifying the voltage by a lock-in amplifier. Function generator applies 1 volt in frequency 3.14 Hz on sample connected to 1 kilo-ohm resistor.
Actuator properties

The current passes through the sample and it be measured by lock-in amplifier at the same frequency as a reference signal which can amplify the desired signal and removes the fluctuation. This system works based on phase-sensitive detection when other frequencies rather than the reference frequency are rejected and do not affect the measurement. The schematic image of set up is shown in fig 4.15.

![Image](image_url)

**Figure 4.15:** Modified set up for surface resistance measurement

The surface resistance based on this method is measured on the samples prepared by physical method after vapor evaporation and sputtering (explained in 3.3.3) and samples by chemical reduction (explained in 3.2.1) to compare the conductivity.

The result comes in table 4.3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fabrication method</th>
<th>Surface resistance(ohm/sq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample $V_8$</td>
<td>Vapor evaporation</td>
<td>1.52</td>
</tr>
<tr>
<td>Sample $V_9$</td>
<td>Vapor evaporation</td>
<td>3.58</td>
</tr>
<tr>
<td>Sample $S_{10}$</td>
<td>Sputtering</td>
<td>12.85</td>
</tr>
<tr>
<td>Sample $S_{11}$</td>
<td>Sputtering</td>
<td>4.03</td>
</tr>
<tr>
<td>Sample $S_4$</td>
<td>Chemical reduction</td>
<td>43.86</td>
</tr>
</tbody>
</table>

**Table 4.3:** Surface resistance of samples made by different methods

- sample $V_8$: patterned polymer + 5nm Titanium + 45nm Au
- sample $V_9$: patterned polymer + 5nm Titanium + 50nm Au + 5nm Titanium + 400nm Aluminum
- sample $S_{10}$: patterned polymer + 20nm gold + 80nm Pt
-sample $S_{11}$: 20nm gold + 80nm Pt

-sample $S_4$: micrometer Pt

Based on results, sputtered sample on patterned polymer has more surface resistance than flat polymer. Also for evaporated samples, surface resistance of $V_8$ is smaller than $V_9$ which shows the outer metal layer has important role in surface conductivity of samples. Here Au is more conductive than Al which cause less surface resistance. For the samples prepared by chemical reduction, the variation of surface resistance is less than 5% which shows good comparable values. Then in all previous experiments with samples fabricated by the chemical method, the surface resistance cannot cause a great effect in the final result. Here, just a typical value of chemical fabricated sample is shown in the table.

The surface resistance value does not just relates to metal coverage which known as the important parameter on sample function. It is well known that cracks influence the surface resistance while the conductivity of surface strongly reduced when no significant current is carried through the cracks [8]. But the cracks have an effective role in the possibility of ion transfer which is the main reason of actuating.

Fig 4.16 a and b are presented surface electron microscopy of the sample fabricated by sputtering $S_{10}$ and chemical reduction $S_4$. Despite pt exist on top layer for both samples, $S_{10}$ shows bigger crack size in comparison to $S_4$ which makes it more surface conductive. This effect is reflected in table 4.3 by higher surface resistance of $S_4$.

More application of surface resistance measurement comes in chapter 5 in sensing part.
Figure 4.16: Cracks on surface for sample fabricated by (a) sputtering (b) chemical reduction
Bibliography


Chapter 5

Sensor properties

IPMC has consisted of hydrophilic ionic part and hydrophobic Teflon backbone. The Teflon properties preserve the structure from the chemical reaction and cause solvent molecules just move inside the membrane under drive voltage without mass exchange with the surroundings. This unique ability conserves the ions inside the polymer network and keeps the correlation between ion movement in micro range and sample movement in the macro range which is the basic of actuator and sensor properties.

IPMCs have been used for years, as an actuator and sensor in several fields from engineering to medicine, but recently the combination of both capabilities are considered to produce smart materials which initiates a new field of self-sensing IPMC [1].

The core objective of chapter 5 is to find proper methods for sensing of sample movement while it is actuating. Here, two different systems have been tested to find out the admitted method for self-sensing application of IPMC.

5.1 Sensing method

As discussed in chapter 4, the measurement of IPMC actuating by laser and camera displacement are the simplest techniques for tracking sample deformation. However,
these methods are not convenient in case of complicated movements like twisting or in uncommon environments such as in space or under water. Therefore, new sensing methods for IPMC have been developed considering measurable change on the particular physical or chemical properties of the sample during actuating. At the beginning of this work, the surface resistance of sample has been chosen as a detector parameter while the values of surface resistance on both sides vary by bending. Several drawbacks of this idea were the motivation to investigate new technique of self-sensing base on the electrical behavior of IPMC at different frequency range. Both methods have explained in this chapter by details.

5.2 Surface resistance

As discussed before, the value of surface resistance is related to the number of cracks on the IPMC surface. During the bending, these cracks are widening on one side of the surface and narrowing on the opposite side which leads to an increase and decrease in resistance value. Thus, the distinction of surface resistance from two sides of a sample can be used as a sensor parameter for real-time position. In this work, this new self-sensing method is investigating which can be used while, no drive voltage applied on the sample, additionally, it can measure the displacement simultaneously while the actuator is running [2]. Fig 5.1 shows this variation under bending.

Based on the idea, the surface resistance from both sides must be measured directly during movement, means the existence of two signals in the system. For this aim, the surface of the IPMC strip must be patterned into actuator and sensor parts. To avoid the effect of actuating function on sensor one, sample divided into three different parts, actuator, sensor and shield between them. Figure 5.2 illustrated the sample with the parts. The surface patterned into actuator part to apply electric field and sensor part to measure detector signal during bending and shield parts in between which is a ground conductor.

The sensor and actuator parts by this method are separated while they have different functions. The drive voltage just applied to the middle part and causes
Figure 5.1: Variation of surface resistance in bending

Figure 5.2: Patterned sample with different parts
bending while it takes the other parts with. Then edge parts move under mechanical force and the surface resistance from both sides, changes by this displacement. The resistance difference is measured as voltage in an electrical circuit. These two parts are shielded from each other to avoid cross-talk between the actuator signal and sensor signal as their frequency ranges are similar.

To measure the difference between surface resistances on both sides, Wheatstone bridge has been used which is an appropriate circuit to measure ohmic resistances and small ohmic resistance changes. The original concept of the Wheatstone-bridge is given as follows: two known resistance R are equal and the system operate similarly to a potentiometer when V measures as a non-zero value which shows unbalance between $R_1$ and $R_2$.

Wheatstone bridge components in our system is schematically shows in fig 5.4 when surface resistance on front side assume as $R_1$ and on back side as $R_2$ in original Wheatstone bridge theory.

In this setup, relation between applied voltage $V_0$ and Wheatstone bridge voltage V is given by equation 5.1:

$$V = V_0\left(\frac{R_1}{R_1 + R} - \frac{R_2}{R_2 + R}\right)$$  \hspace{1cm} (5.1)

This formula gives ratio between resistance variety at front side ($R_1$) to back side ($R_2$) in bending when the initial surface resistance (R) at each sides are assumed
equal. To convert the measured resistance to actuate displacement, the resistance ratio is related to length ratio by strain Gauge factor (Gf) in equation 5.2. Where “s” denotes initial values of sensor parts.

$$\frac{\Delta R}{R_s} = Gf (\frac{\Delta L}{L_s}) = \frac{t}{2}K$$  \hspace{1cm} (5.2)

It can be claimed that the change in length of the samples, relates to bending momentum K by considering the sample thickness t. The formula shows how the surface resistance measurement related to sample bending and prove the theory of this method.

As explained before (5.2), to use the idea of using surface resistance for displacement measurement, the sample should have pattern on surface which will explain in the next section.

5.2.1 Patterned sample

The shape of electrode, number of segments and the polarity of electric field define the movement of an IPMC sample. For example, one sample with two separate electrode on each sides can produce twisted motion is shown schematically in Fig5.5.

By controlling the fabrication process and changing the electrode, wide ranges of application are possible especially for self-sensor function. In the case of self-sensor,
the surface electrode should be divided into three parts: actuator, sensor and shield when the area between them should be clean of the metal layer as shown in fig 5.2. These metal-free parts are called wiped area afterward and they must be covered during chemical reduction (explained in chapter 3) to keep the polymer away from the metal particle.

The another possibility to pattern sample is to do the normal reduction on the polymer film and later on the metal layer removes by the physical way like scratching of wiped area [3]. For the first method, some part of polymer strip cover with different materials as a mask. To consider the effect of mask type, two samples by different masks have been prepared. The masks were Polyamide in tape shape and Tippex in liquid form. In addition, one sample with physical scratch method was made to compare the efficiency of all methods. All prepared samples are explained as follow:

Sample 1: This sample is made by normal chemical reduction according to steps which explained in 3.3 and afterward, the subulate cutter has removed the electrode metal from wiped parts. Electron microscopy shows, lifting the metal penetrated inside polymer during reduction is not possible without damage to polymer structure.

Sample 2 and 3: Samples are patterned by covering the wiped parts with mask during chemical reduction. Tippex liquid as a mask is used for sample 2 and the masking process is repeated three times to achieve the best coverage. One layer Polyamide film covers the wiped area of polymer for sample 3. Both samples are kept fix by the holder is shown in fig 3.7 during reduction process to make uniform protection effect. Fig 5.7 is shows SEM measurement of sample 2 and 3.
Figure 5.6: IPMC sample after scratching in two scales

Figure 5.7: IPMC sample with various masks
Images are shown clean coverage and acceptable result for both masks. These two samples are selected as patterned IPMC for the self-sensor test by Wheatstone method.

5.2.2 Self-sensing by surface resistance

Section 5.2 describes the idea of using surface resistance at both sides of IPMC sample as a sensor parameter to detect the actuating. The measured voltage at Wheatstone-bridge is considered as sensor signal when equation 5.2 proves the relation between this measured parameter and momentum of the sample. The sensor signal by this method can be measured simultaneously during bending of the actuator part of the sample. The admitted result should be in good harmony with laser displacement measured base on method explained in section 4.3.

The plot in fig 5.8 shows three signals: applied voltage to actuate part, signal measured on sensor part and signal of laser displacement. The plot shows at first look, same frequency of periodic signal for self - sensor and laser.

![Figure 5.8: Sensor signal for patterned sample](image)

To investigate the self - sensing method more accurate, the sample stimulated mechanically during normal actuating. The sensor signal should be able to show this disturbance on regular bending. The results of this test, are plotted on fig 5.9,
which shows sensor signal follows the actuator signal rather than laser displacement under this situation. The result exhibit power of cross-talk that means the actuator signal affects strongly the sensor behavior.

Cross-talk is the coupling of energy from one line to another line in near distance via mutual capacitance. The phenomena create an undesired effect in two parallel channels of a transmission system. In self-sensing system, actuator signal surrounded by sensor signal which is supposed to be protected from each other by a ground conductor of shield part but the results have clearly demonstrated the effect of this noise. Far from the noise problem, there are other drawbacks related to this method.

The main drawbacks of using surface resistance as a sensor parameter are complicated fabrication process which is required patterning or adding several contacting points to sample. The second drawback is that a large area must be devoted to the sensor and the shield parts which result into smaller actuate part and lower bending force. Additionally, reserving the parts for sensor and shield limits the miniaturizing process on sample size which is desirable in micro application of IPMCs. These disadvantages plus cross-talk effect prove that a better self-sensing system is required.
5.3 Resistance across the sample

In an equilibrium situation, ions inside an IPMC sample are distributed uniformly all over the area. An applied electrical potential, causes ion redistribution followed by bending (deformation) of the strip as the result of interaction forces. Additionally, when IPMC is externally stimulated, the ions inside the membrane move and collect on the electrodes and generate an output voltage. Based on this fact, a new sensor technique was designed. In this technique, instead of measuring the resistance on the IPMC surfaces, the resistance across the sample is measured [4].

Figure 5.10 shows schematically cations flow under external force with water molecules in micro channels which calls mechanical-to-electrical transducer.

![Figure 5.10: Cation flow under external force](image)

These cations inside the polymeric microchannel are rolled up by the external mechanical force and the ions flow produces a cation current which is measurable with an appropriate device. Additionally, when the movement is blocked the current value decays to zero as a respond to the disturbance on displacement. By using this idea, the actual position of the sample and the previous position must be recorded to sense the displacement. The challenge with this technique is that the actuating
Voltage and sensing voltage in the system are not in the same order of magnitude (sensor is much smaller), which means it is not easy to use this sensing technique while the actuator is running. This problem can be overcome if two IPMC strips are attached to each other, and one is used as the actuator and the other as the sensor. However, cross-talk between actuator and sensor and the fabrication process increases the complexity of this method. Our new technique can measure disturbance with and without actuating voltage by avoiding the cross-talk noise without need for pattern on the sample. The idea for this method comes from the performance of IPMC in different frequency ranges that explained in next section.

5.4 Electrical behavior of IPMC

Electrical behaviors of IPMC in the frequency regime of less than 10 Hz (actuating frequency) and higher than 1 kHz are distinctly different. This behavior is according to the inertia of ions which defines their movements depended on to frequency. At fast frequency (typically above 1 kHz), ions cannot follow the electric field direction and mostly behave as immobile charged particles. In this range, only electrons contribute to the electrical properties of the sample without any actuating effect. The variety of response for ions and electrons to the electrical field plus the capacitor character of IPMC results in a non-linear and frequency-depended correlation between current and voltage. By increasing the frequency, the non-linearity decreases until it vanishes entirely and Ohm’s law can be used to describe the resistance behavior of IPMC [5]. Thus, apart from the ion concentration and sample dimension, the resistivity of IPMC across the membrane also depends on the frequency, and one can use this property to design a self-sensing technique. The resistance behavior of IPMC is shown in fig 5.11.
Figure 5.11: IPMC electrical behavior in different frequency from simulation
5.5 Electrical circuit design

By considering the frequency dependency of IPMCs, following circuit is designed to measure the change in the resistance across the IPMC by bending or by external stimulation. The experimental setup was composed of opto-electromechanical measurement instruments consists of set up explained in section 4.3 plus a part for sensing function shows in fig 5.12.

![Figure 5.12: opto-electromechanical set up](image)

In this setup, the sample hangs in the air when the actuator voltage is applied to metal electrodes on both sides and the bending value is measured by a laser displacement sensor as a reference signal which has been used before to characterize the IPMC performance.

The sensor part of the setup is consisted of IPMC and a small external resistance. The high frequencies of few kHz, applied to sample and external resistance (around 1 Ohm) when any change on sample resistance as result of bending or external displacement, changes the voltage drop on this external resistance [6]. Additionally,
Sensor properties

A step motor with a plastic handle is employed to bend the sample mechanically while speed and value of push are controlled for each stimulation. The Lab view program with multichannel input records the voltage amplitude for the actuator, sensor and drop voltage on the external resistor. The actuator and sensor voltages were consequently generated by a two-function generator of HM8130 and TOE 7404 at different frequency ranges which are necessary for simultaneous sensing and actuating. Based on this setup, the total resistance in sensor part of the circuit can be written as equation 5.3.

\[ R_{total} = R_{IPMC} + R_{External} \]  \hspace{1cm} (5.3)

The current passes through the sample is the same for the external resistance. Then

\[ V_{total} = V_{IPMC} + V_{External} \]  \hspace{1cm} (5.4)

The \( V_{total} \) is sensing voltage applied at the high frequency and it is constant value then the correlation between the voltage on IPMC and voltage measured on external resistance is clear. The variety on the amplitude of \( V_{External} \) is our sensor parameter which is related to sample displacement. This variation on amplitude is small value affected by electrical noise in the system. A lock-in amplifier (Stanford system, SR830 DSP) is used to recover this signal in the presence of actuate signal and provide high-resolution measurements on sensor signals. A lock-in amplifier, in common, uses a technique known as phase-sensitive detection to amplify a signal at a specific frequency. The function generator for the sensor can be isolated from the actuator one by using two capacitors, while the capacitor passes a high-frequency but blocks the low-frequency of the actuator. One the other hand, to protect the actuator system from the sensor two inductors are employed to stop the high-frequency voltage but inductor act like simple resistors for low-frequency voltage. The schematic image of the setup in presence of all elements comes in fig5.13

To compare the sensor signal by this method to laser displacement as a reference, series of measurements are planned at different frequency. Fig 5.14 is illustrated these results compare to laser displacement measurement.
Figure 5.13: Schematic image of set up

Figure 5.14: Sensor signal and laser signal at different frequencies
Sensor properties

At frequency 0.25Hz when the amplitude of applied voltage sweeps the values from 20 mv to 3.5 v, both sensor signals present a similar trend. By increasing the frequency to 0.5Hz sample displacement diminishes extremely in compare to laser detector. This diminishes also expected from the previous test has done in chapter 4. The detection of smaller displacement conflict between our sensor signal and laser displacement is higher. This circumstance is more obvious at bigger frequency but as results show when the IPMC displacement is significant usability of this method is clear.

5.6 Detection of external stimulation

In the previous section, we explain that the sensor signal base on our method is in good harmony within laser displacement but to use this signal as a smart detector it is necessary to study special situations:

The IPMC response to constant drive voltage when the sensor circuit is involved and when is completely disconnect must show similar performance. Thus the bending of IPMC both in the presence of the detecting system and when the detector was totally detached are measured. The result in fig 5.15 shows where the bending is significant (voltage more than one volt); the change in the bending in the presence of the sensor is very small so the effect of the sensor can be ignored.

The sensor signal should be stable and usable to measure the actuation when the drive voltage is on and external stimulation and when the drive voltage is off. In addition, if any external mechanical force disturbs the normal bending, sensor signal must be able to detect this disturbance on normal actuation. This effect improves the application of IPMC as artificial muscle when the self-sensor function can sense the environment and behaves as a smart actuator.

The mechanical disturbance on the sample applied by two types of deformations with and without electrical stimulation: impulse and motor (with a constant speed) deformation. The response of our sensor and laser displacement to the both external mechanical disruption are shown in fig 5.16 and 5.17 while the actuating voltage is off and on respectively.
Figure 5.15: Effect of sensing process on IPMC function measured by laser displacement.

Figure 5.16: The response of sensor and laser to external impulse while actuator is off [4].
Sensor properties

Figure 5.17: The response of sensor and laser to external impulse while actuator is on [4].

The laser displacement is calibrated for a very high resolution, thus sometimes the bending is out of the range for the laser sensor and shows a saturation effect. Our sensor does not have saturation and limitation on the measurable range as an advantage compared to the laser sensor. The detected signal for the impulse has presented the deformation easily even when the actuator is on, and its sensitivity does not change compared to when the actuator is off.

Periodic rectangular push with constant speed (part b in fig 5.16 and 5.17) are illustrated that the sensor could follow the movement from start to end with the same rate. The plots are obviously shown, the sensor is not detecting any movement when the IPMC film is kept in the new position for around 15 s at the end of each push. Figures 5.16 b shows that the sensor signal is returned to the previous position before pushing and no hysteresis effect is observable after stimulation. This result has achieved after modification on setup to completely isolate the actuator and sensor circuits from each other by using inductor and capacitor explained in 5.5. In this situation, both sensor and the actuator systems are worked independently in the experimental conditions of these tests. Figures 5.16 and 5.17 (part a) show that our
sensor is less sensitive to the displacement compared to the laser sensor. However, we believe that this limitation can be overcome by modifying the experimental set-up better.

5.7 IPMC as a sensor

The previous section presented IPMC function as a self-sensor actuator by using our new method. This section has explained the possibility of using them as distance sensor and speed sensor with same method. As mentioned before in section 5.3, sample resistance across the polymer changes by ions redistribution. This ion flow normally is the result of IPMC tip movement under electrical drive signal or under mechanical force, then resistance measurement should be able to detect every variation on regular condition (electrically or mechanically). The IPMC cantilever hangs up in the air when automating step motor pushes it in one direction step by step. All parameters of the step motor, like speed, distance and stop time between each step are controlled by software. Fig 5.18 shows this mechanical force on the sample, stop movement, pause time in between and next push. Based on this plot, our sensor signal is able to follow the movement in harmony with laser displacement.

Furthermore, when drive voltage on the sample is zero and it works just as a sensor, our method is able to detect rectangular periodic push. Here, the important questions are: the different push distance and faster or slower push are detectable by this method? and is there any limitation on detectable minimum distance?

To answer these questions, series of measurements have been done with step motor at different distances and by different speeds. The results are presented in fig 5.19 and 5.20.

The figure 5.19 clearly shows the linear relation between the sensor signal and the displacement value. The minimum value of movement which this method is able to detect is around 0.2 mm while the sensor signal for less displacement than this value is small and noisy.

Figure 5.20 is the relation between speeds of the stimulated pulse with sensor signal in constant displacement. The sensor signal cannot follow high-speed pulse
Sensor properties

Figure 5.18: Mechanical regular force on IPMC sample

Figure 5.19: Mechanical regular force on IPMC sample in different value
which is detectable in the plot due to nonlinear behavior. As the ions participate in the sensor signal, it can be expected that their ability to respond to the stimulation is limited to the certain range.
Bibliography


Chapter 6

Simulation

In this chapter the function of IPMC at different condition is simulated by using equal electrical components in a Matlab Simulink. The simulation with Matlab is an useful tool for analyzing the system to develop knowledge on the electrical behavior of sample in relation with the variety of effective parameters.

Before starting the simulation, the electromechanical behavior of IPMC should be simplify to express by basic electronics component. Proper choosing of this components, have direct effect on accuracy of result. Different equivalent circuits are described in literature including Shahinpoor model [1], Kanno-Tadokoro model [2], Bar-Cohen model[3] and Paquette model [4].

These models are considered the IPMC function as RC circuit or RLC circuit to explain real phenomena in some specific situations but they can not be used in general case. Here we are used the RC+Diode model for the frequency dependency because classic RC model is not realistic in voltage lower than actuating threshold. Additionally, for the RLC model, the voltage dependency has mismatch behavior to the real sample. At this stage, the output signals from simulation and experiment are compared to check the compatibility of selected model. The successful simulation can be helpful to optimize the sensing signal and calibrate each component, especially for miniature IPMC strips.
6.1 Equal electrical model

The IPMCs structure consists of two conductive metal layers on a polymer surface then the electrical action of them are basically capacitor–resistance component. Additionally, the ions redistribution under the electric field is produced a nonlinear impedance should be considered in the simulation model. Therefore, the equal structure includes the capacitance, surface resistance of IPMC, variable nonlinear impedance and in addition, the electrical conduction across the polymer membrane. It also should consider a voltage threshold in which below that the IPMC shows no reaction to the applied voltage. Some simulation models [5] are also included an inductor to simulate the actuate response time. However, in the frequency range of our sensor method, the damping attenuation of the RLC branch will be too big, which means a very fast relaxation of the sample is lead to a non-physical response for IPMC, thus an RC model was preferred over RLC. Section 5.4 was explained IPMC function at different frequency range which is related to frequency dependency of ion or electron currents. Ionic current is the resultant of cations movement from the anode to the cathode in direction of electric field. At high-frequency signals, ionic motions are strongly decreased, since the cations, surrounded by water molecules, cannot move fast enough. The electronic current is a flow of electric charges at membrane between two electrodes and the value is significant if the energy of drive voltage is higher than actuate threshold. Additionally, the physical structure of the IPMC similar to simple capacitor causes displacement current as well.

Here, the equivalent circuit contains two branches, one of them denotes the electronic and the other indicates the ionic current at the IPMC function. The ionic branch consists of a resistance, a capacitor, and two diodes. The diodes are used in order to reflect the minimum necessary voltage for actuating. The electron current and ion current have various sensitivities to frequency, thus two capacitors with different capacitance should be employed to simulate this response [6]. Figure 6.1 shows the schematic image of the simulation model.
6.2 Simulation model in set-up

The equal electrical component for IPMC should be replaced in set up which shows before in fig 5.13 to simulate the experimental system. In this system, the values of the inductors and capacitors of the circuit should be modified in order to completely isolate the actuator and sensor circuits from each other. The impedance of the inductors and capacitors can be written as follow:

\[ Z_L = i\omega L \]
\[ Z_C = \frac{1}{i\omega C} \]

\[ Z_{total} = Z_L + Z_C = i\omega L + \frac{1}{i\omega C} = \frac{1 - LC(\omega)^2}{i\omega C} \quad (6.1) \]

The circuit has two power suppliers to provide low and high frequencies and sample located in the middle line. To shield each power supplier from another one, the following equation should be valid when the total impedance at high(\(\omega_H\)) and low(\(\omega_L\)) frequencies are equal:
\[ Z_{\text{total,High}} = Z_{\text{total,Low}} \]

\[
\frac{1 - LC\omega_H^2}{i\omega_HC} = \frac{1 - LC\omega_L^2}{i\omega_L'C} \quad (6.2)
\]

Then the inductors and capacitors should be chosen based on high and low frequencies for each simulation test which is presented by the following equation:

\[
LC = \frac{1}{\omega_H\omega_L} \quad (6.3)
\]

High frequency means frequency range which IPMC has sensor application and low frequency is actuator range. Final simulation model which has been made in Matlab Simulink is shown in Fig 6.2.

### 6.3 Simulation result

For the actuating range of voltage and frequency (typically voltage less than 3 V and frequency less than 2 Hz), simulation model should have results comparable to experiment. Figure 6.3 to 6.5 present the output of the lock-in amplifier for the simulation and experimental set-up in comparison to the laser displacement as a reference signal. The measurements are repeated for three different frequencies of 0.25 and 0.5 and 1 Hz and all data are normalized to laser displacement values.

Our simulation results are indicated that assumed model of RC+Diode has consistency performance to real IPMC in the possible frequency range for applied voltage from almost zero to maximum value. The plots compare measurement by our new sensing method and laser displacement which are two methods to study the sample function. By using this simulation model, one is able to choose appropriate parameters of self-sensing technique and shield betterment which is important in work with IPMC especially with a miniaturized sample.
Figure 6.2: Simulation set up in Matlab Simulink
**Figure 6.3:** Simulation experiment - laser displacement (0.25Hz)

**Figure 6.4:** Simulation experiment - laser displacement (0.5Hz)
The simulation chapter is presented as the last chapter but practically, this step was the first evaluation to design the electric circuit is used in sensing method. To have this harmony between the performance of sample and simulation model, the elements of an equal electrical model (fig 6.1) should have values related to resistance and conductance of sample which is different from sample to sample. The elements of simulation model such as $R$ and $C_1$ and $C_2$ are selected based on the electrical behavior comparison to real sample at various frequency ranges. The only elements can be measured directly, is surface resistance which is explained in 4.4.

The electrical behavior of IPMC was explained in section 5.4, is demonstrated the variety of current-voltage relation from nonlinearity to the ohmic linear. The specific frequency which one sample is started to show the linear behavior is distinct value for each sample which can be used as a scale to select components of simulation model. The current and voltage values are recorded for each sample and simulation model and the frequency sweep ranges from few hundred to few kHz. When the result shows qualitative similar values the selected model is an equal electrical component to the sample.
The output from the lock-in amplifier for both experiment and simulation are measured, rescaled and plotted for different frequencies in fig 6.6 which can be used as standard test to choose the simulation model.

![Figure 6.6: Frequency dependence of resistance for IPMC and simulation model](image)

The plot is clearly illustrated exponentially decrement of sample resistance by increasing the frequency for both simulation and experimental in good qualitative agreement. Although, at the high frequency the rate of decreases are not similar for them while the experiment results have a faster rate of decay from perfect exponential of simulation. The measurement error for our sensor circuit can be the reason of this mismatch because the resistance value of the sample at such a high frequency is really low. By choosing an appropriate component, advantages of the simulation are in hand especially for next step to miniaturize the sample size.
6.4 Miniaturizing of sample

Credible simulation with proper result provides the possibility to calibrate the setup related to sample properties. The importance of this procedure comes from this fact that the sample size is critical parameter to characterize the capacitance or resistance value and surface resistance of IPMC sample. By simulation, the relation between sample size and sample components achieves which guaranties the results after each step of size reducing.

To miniaturize the sample size, at each step prior size reduced to half amount and new sample tested by the setup with constant voltage and frequency of actuator but with specific sensor combination to attain the best sensitivity of the sensor. The miniaturized samples are 1 (full size) and sample 2 (1/2 size) and then sample 3 (1/4 size) when for all of them the length of sample kept constant to have the same relation of bending and curvature (explained in section 4.2). The bending values for all three samples are shown in fig 6.7.

Figure 6.7: Displacement compare of miniaturized sample at frequency 1Hz
It is clear that the miniaturized sample after each step shows less bending even if the length of all sample are equal the membrane size and amount of ions inside are different for samples. The plot is exhibited a linear relation between displacement decreasing and sample size. The corresponding miniaturized models for sample 1 and 2 and 3 in the simulation are presented similar descent in compare to the IPMC measurement for these samples. The results are presented in fig 6.8.

![Graphs showing linear decrease of actuating by size](image)

**Figure 6.8:** Linear decrease of actuating by size

When the bending degrades by reducing the sample size, it is critical to improving the set up when the best signal for a miniaturized sample is required.

Our measurements have proved the dependency of sensor signal sensitivity to the frequency which is chosen for sensor circuit. That means, at certain actuator parameters and certain sensor voltage, when the sensor frequency sweeps the range of linear behavior from few kilohertz threshold, there is a distinctive frequency which the sensor signals has maximum value and best sensitivity. These especial frequency changes from sample to sample and strongly depends on surface resistance. For sam-
ple 1, 2 and 3 surface resistances are measured by Van-der-Pauw-method explained in 4.4 then this surface resistance values in simulation model replaced instead of the resistance R. The results of equal simulation component by this element in different frequencies are recorded to find out the frequency start point of linear electrical behavior. Base on this idea, for each sample, is possible to find the range of linear behavior and best sensitivity of sensor signal which is strongly necessary for miniaturized samples. The surface resistance values and estimation on the frequency by simulation to have the best result and sensitivity comes in table 6.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface resistance (ohm)</th>
<th>Frequency range base on simulation(KHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>55.6</td>
<td>45 – 50</td>
</tr>
<tr>
<td>Sample 2</td>
<td>72.2</td>
<td>50 – 55</td>
</tr>
<tr>
<td>Sample 3</td>
<td>122</td>
<td>55 – 60</td>
</tr>
</tbody>
</table>

Table 6.1: Surface resistance and required frequency

At next step, the amplitude of sensor signals is recorded when frequency sweeps the estimation range from table 6.1. For this series of test, the applied voltage to the sensor circuit for all samples is kept constant as well as actuator voltage and frequency. The results of these measurements are presented in table 6.2 which shows the maximum sensitivity of detection at constant displacement for each sample. Finding the distinctive frequency for each sample which they have a maximum value at constant actuate parameters guarantees the quality of sensor signal for a miniaturized sample.

Table 6.2 proves that sensitive strong sensing signal, occurred at the distinctive frequency for each sample. This especial frequency is the frequency which the resistance across the IPMC is in the range of surface resistance. In the simulation model, the value of surface resistance helps us to find the frequency of the best sensitivity. This useful technique can be applied for all electroactive polymers such as ionic polymer gel and elastomer while the electrical response of them is related to charged particle. In the experimental setup, maximum sensitivity is achieved at the above-mentioned condition. In the case of IPMCs, after any change in sample properties by the help of surface measurement and simulation, set up can be easily modified and used in the proper condition.
<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
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<th>Sensor(v)sample2</th>
<th>Sensor(v)sample3</th>
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*Table 6.2: Maximum sensor signal at distinct frequencies*
Bibliography


Chapter 7

Summary and further works

IPMCs as a smart material are growing field in science and technology. The motivation of this work was to develop the knowledge in fabrication and characterization method, additionally, combining the actuator and sensor function of IPMC. The combination of both operations leads to self-sensor IPMC which has application in smart robotic and bio-mimic artificial live organisms.

In chemical fabrication method, Nafion film under a multi steps chemical process turns to the metal composite to make two electrodes on both sides of the polymer. The primary process inserts Platinum deep inside the membrane to provide continues conductive layer and increase the electric field-ion interaction. Then, the secondary process increases the metal thickness on the surface and improves the actuating function.

As new fabrication approach, physical method was developed to reduce the time and complexity of the sample preparation and increase the control on involving parameter in fabrication steps. For this aim, the regular hole pattern on the surface is constructed by electron-beam which is necessary for penetration of metal inside the polymer.

As the polymer-metal adhesion is week, different treatments were employed to enhance the stability of metal layer on the surface. Finally, the metal layer is deposit by sputtering and thermal evaporation techniques. The sputtered samples are shown more stable metal layer in swelling step and under the electric field.

In the characterization process, electron microscopy, contact angle measurement,
Dektak profilometer and laser confocal microscope provide information about fabricated samples. This information is used to improve the quality of each fabrication steps and final products. The surface morphology and thickness of metal layer were measured by SEM images. In parallel, TEM images have proved the penetration of metal particles in the polymer film. The created structure by electron-beam was analyzed by Dektak profilometer and laser confocal microscope. The regularity of pattern and depth of holes were detected after each patterning process. The contact angle shows the impact of each treatment process for improving the metal-polymer adhesion.

A new setup has designed to measure the actuating behavior of samples, in addition, to sense the motion simultaneously. The setup is consists of two function generators, one applies desired actuating voltage and frequency to metal electrodes while the laser displacement is measured the movement by using reflection point and angle. The other voltage applied as sensor signal on the sample while the variation of amplitude can be used as a displacement sensor as well when it must show similar results in compared to laser.

The chemically fabricated samples have more displacement in comparison to physically fabricated samples. One of the factors involved in these results is the numbers of cracks on the surface electrodes which has visualized by electron microscopy. Furthermore, cracks populations have increased the surface resistance value which has measured for samples to sample to prove the importance of crack effect on IPMC performance. The chemically fabricated samples have the higher density of crack which is the place for transferring of ions between the inside of polymer film and environment ionic liquid in swelling step.

To use IPMC as a self-sensor, the properties of IPMC which change by bending were used as a detector parameters. These possible properties in this thesis are surface resistance and bulk resistance. The surface resistance value varies by bending and can be used to detect the displacement to combine both actuator and sensor application with some modification. This technique is feasible by patterning the sample to divide the functional parts and grounded shield between them which is necessary for correct function without cross-talk noise. In addition, a new and effective method for self-sensing was developed to measure the bending movement plus the external disturbance during bending while needs no requirements on sample
shape modification.

The basic idea of our new technique is the variety of IPMCs electrical behavior in different frequency ranges which guarantees the actuator and sensor function separately and simultaneously. The sample displacement changes the resistance across the sample which is detectable in the proper frequency range. The most advantage of this method is that the sample does not need the pattern or especial modification. The low and high frequencies can be applied on a strip of IPMC simultaneously while by the help of an especially designed circuit and a sensitive lock-in amplifier they are not affected each other.

To improve the efficiency of the designed electronic circuit, simulation by MATLAB Simulink was tested possible electronic elements combination. Here, surface resistance and frequency depended measurements are the guideline to choose the proper values for equal electrical components to simulate the IPMC sample.

The future works are developments of the physical fabrication method to prepare the IPMC sample in micro size and improvement on the sensitivity of sensor signal. These two further steps result into a successful miniaturizing process and it is the aim of application in biology and medicine. Moreover, the results are proved the effect of crack on the surface for the better function which means more cracks increases the ion density inside the membrane. Hence, further work is adding the metal layer on primary layers step by step in sputtering procedure to achieve more possibility for crack on them. In this situation, the sample is able to uptake more ion in swelling step. In addition to keep them stable in the membrane, encapsulation process is suggested at the end. All proposed idea can improved the sample lifetime and function in proper way.
Appendix A

MATLAB programming

The Matlab software was used to calculate the mean value on each measurement. Several code was developed to calculate the maximum and minimum of sensor signal. Furthermore, matlab simulink by using equal electrical components investigates IPMC behavior at different condition.

```matlab
1 clear
2 clc
3 format longG
4 %loading file
5 load s25t34.txt '-ascii';
6 Data=s25t34;
7 N=400000; % number of data in each column
8 %HF0=A6t9(1:N,1); % LF0=Data(1:N,2);
9 L0=Data(1:N,3);
10 %S0=A6t9(1:N,4);
11 f=0.5; % frequency
12 fs=8000; % record rating
13 % averaging to reduce noise
14 A=100;
15 x=round(A/f);
16 U=round(N-x);
17 %for j=1: U;
18     %HF(j)=median(HF0(j:j+x));
19 % end
```
for j=1: U;
LF(j)=median(LF0(j:j+x));
end
for j=1: U;
L(j)=median(L0(j:j+x));
end
% for j=1: U;
%S(j)=median(S0(j:j+x));
%end
% Pick to pick

for k=1: round(46*f) % time of measurment
msignal=min(LF(1,k*X:(k+1)*X));
Msignal=max(LF(1,k*X:(k+1)*X));
signal1(t,:)=Msignal-msignal;
mlaser=min(L(1,k*X:(k+1)*X));
Mlaser=max(L(1,k*X:(k+1)*X));
laser1(t,:)=Mlaser-mlaser;
t=t+1;
end
sensor=mean(signal1);
laser=mean(laser1);

fft=-fs/2:fs/(U-1):fs/2;
% FHF=abs(fftshift(fft(HF)));
FLF=abs(fftshift(fft(LF)));
FL=abs(fftshift(fft(L)));
%FS=abs(fftshift(fft(S)));
%plot
% figure,plot(ff,FHF)
% title('HF')
figure,plot(ff,FLF)
title('LF')
figure,plot(ff,FL)
title('Laser')
%figure,plot(ff,FS)
%title('S')
MATLAB programming

```matlab
61 figure, plot(Data);
```
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1. Direct Patterning of Ionic Polymers with E-Beam Lithography. MRS Advances, 1(01), 45-50, 2016


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5. Self-Sensing Ionic Polymer Metal Composite, EuroEAP, Sweden, Linköping, 2014


7. IPMCs as a artificial muscle, Deutsche Physikalische Gesellschaft, Regensburg 2013