Fabrication, Characterization and Application of Ionic Polymer Metal Composite

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Abstract: ***The Ionic Polymer-Metal Composites (IPMCs), which are electroactive polymer from the family of smart materials. These electroactive polymers hold strong properties for versatile sensing and actuating applications [1-3]. IPMC consist of a fluoropolymer ion exchange membrane like Nafion™-117 by DuPont, sandwiched between two conducting noble metal layers, such as platinum, gold etc. The current states–of- art procedures to fabricate IPMC, like chemical plating methods are time-consuming, complex and expensive. Hence, mechanical plating techniques like physical vapour deposition also known as Sputter coating is the most commonly used deposition technique [3]. This paper demonstrates the fabrication procedure and operational characteristics of IPMC, which give scope to use this as transducers.***

Keywords: Ionic Polymer Metal Composite, Scanning Electron Microscope, Sputtering, Relative Humidity

1. Introduction

IonicPolymer Metal Composites (IPMC) which are electroactive polymers are capable of electromechanical and mechanoelectrical response to applied voltage and mechanical deformation respectively [1-3]. It consists of thin ionomeric membrane sandwiched between metal electrodes. The thin membrane is of Nafion® from Dupont™ is perfluorinated alkenes with short side chains terminated by sulphonate SO3- ionic group and a cation, such polymers have a linear backbone with no cross-linking and fixed ionic group[3].

The two main properties of IPMCs as its low activation voltage and a large bending strain due to the movement of cations in polymer matrix give potential to use as transducers. There are various manufacturing techniques for fabrication of IPMCs as chemical plating, physical metal loading, solution casting, hot pressing and physical vapour deposition [3]. Among these methods, physical vapour deposition method [19] gives the uniform thickness of electrodes, low cost, shortest processing time, good actuation and it can also be used as integration with other methods [6] for better performance.

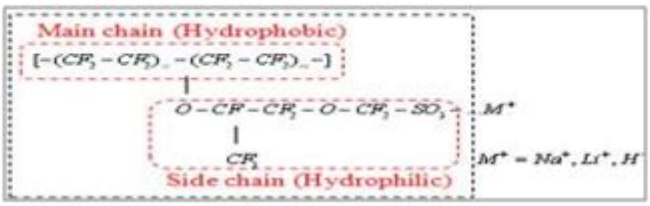

Figure 1: Chemical structure of Nafion™-117 membrane

The sensing and actuation behaviour of IPMCs depend on basic properties as water holding capacity, sheet resistance, type of cations in the polymer matrix[14].IPMCs are widely used as biomimetic robotic distributed sensors, and actuators as transducers and artificial synthetic muscles. In this paper, the main aim is to fabricate IPMC for humidity sensor [20].

2. Fabrication

IPMC is fabricated with Physical Vapour Deposition method which is based on sputtering mechanism. The procedure of fabrication is given as:

2.1 Preparation of Sample and Pretreatment

Nafion™-117 membrane of size 5cm×5cm×200 µm is cut by-YAG laser cutting machine. Nafion membrane was roughened by P-3000 grit size of sandpaper. During roughening uniformity should be maintained. After roughening images were taken by Scanning electron microscope (SEM) which shows microfeatures are created after roughening.

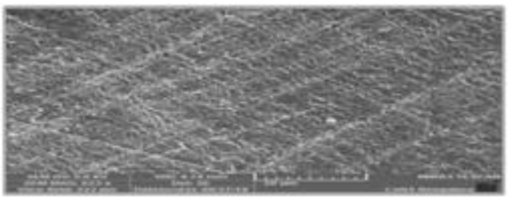

Figure 2: SEM image after roughening (Nafion-117 membrane)

During roughening, the membrane was contaminated and there were oil and organic pollution on the membrane surface. To clean this sample membrane was ultrasonicated for half an hour in acetone. For penetration of more H+ ions in the polymer, the matrix sample was boiled in 2M HCL acid at 90°C for 30 min. H+ ions are responsible for cation movement during Sensing or Actuation. The sample was boiled in DI water for 30 min to extract the residual acid from the membrane. The sample was dried in the U-V Ozone cleaner. It also creates some nano features on the surface.

2.2 Deposition of electrode layer

Finally, after the pretreatment process sample was put into the Dual Magnetron Sputtering Machine Set-up. In this Firstly, a titanium layer of thickness 150nm (each side) is deposited on a membrane which acts as the adhesion layer, then gold of thickness 750nm (each side) is deposited on a membrane. Proper temperature (room temperature) and vacuum (10-5 bar) condition should be maintained during deposition. Samples were cut into 4 small pieces. To improve the sensing and actuation property of these IPMC samples were immersed in 1N LiOH solution for 2 days and rinse with water.

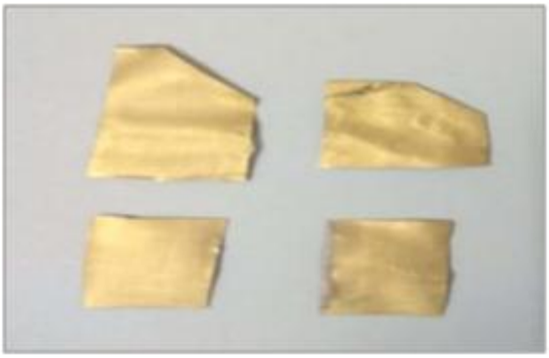

Figure 3: Fabricated IPMC samples

3. Characterization

The Characterization of Nafion™-117 membrane and fabricated IPMC is done to understand the basic properties of Nafion membrane and IPMC transducers.

3.1 Importance

Characterization of Nafion™-117 is done to understand the effect of various factors such as water holding capacity and ion exchange capacity of membrane on the basic mechanism of ion exchange which is responsible for sensing and actuation to analyze the morphology of surface of IPMC after deposition and change in strength of membrane after depositing electrodes over it characterization of IPMC is performed.

3.2 Measurement of Water Holding Capacity

Water holding capacity is responsible for the movement of cations in the membrane. High water holding capacity of Nafion™-117 membrane is an indication of good sensing and actuation performance.

To find water holding capacity a pre-weighed membrane was immersed into distilled water at room temperature and at temperature of45°C for different intervals of time (as 2, 4, 6, 8, 10 hours). After every interval membrane was removed from the hot plate, wiped and its weight was measured. Change in weight of wet and dry membrane gives the water holding capacity in percentage. The water holding capacity of Nafion™-117 membrane form experiment is 19.047%.

The graph shown in figure-4 indicates that at high-temperature membrane absorb water faster than that of water absorbed at room temperature. After 10 hours of membrane absorbs the maximum amount of water and become saturated. In this graph the water holding capacity is taken on Y-axis and time is taken on X-axis.

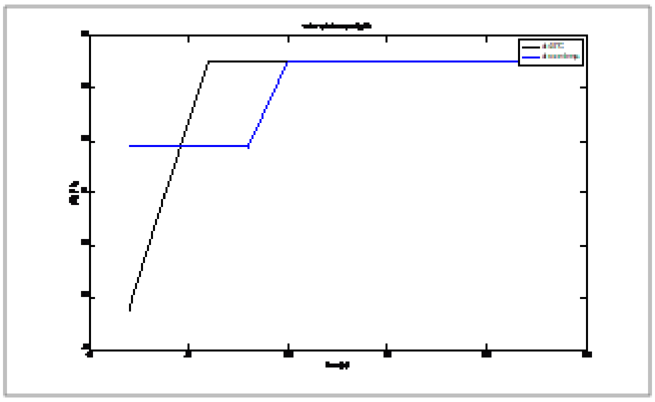

Figure 4: Measurement of water holding capacity of Nafion-117 membrane

3.3 Measurement of ion exchange capacity (IEC)

It indicates the amount of cations or counter ions a membrane can store. High concentration of cations is responsible for the good performance of IPMC based sensors which lead towards its high sensitivity. Ion exchange capacity is determined by acid-base titration.

In this Nafion membrane is immersed in 0.1 N NaOH solution for 24 hours, then10 ml solution is extracted and Phenolphthalein is added to separate acid from the base. After this process, 0.1N HCl is added until the solution becomes neutral.

On comparing the amount of HCl required for titrating NaOH solution before and after immersion in the Nafion membrane, it is found that less amount of HCl required after immersion. The Na+ ions exchanged with H+ ion of Nafion membrane. On taking the difference of volume and Normality of HCL required before and after immersion of the Nafion membrane and dividing it by weight of the membrane. The IEC of the Nafion membrane is 1.434 mEq. /g (weight of Nafion membrane is taken as 0.023g).

Figure 5: Measurement of IEC of Nafion™-117 Membrane

3.4 Tensile Strength

The young modulus, tensile strength and tensile strain of ionic membrane were determined using a Tinius Olsen H25KS universal tensile testing machine. Mechanical properties such as tensile strength and young modulus strongly influence the fabrication conditions of IPMC and also the durability of transducers. The engineering stress-strain diagram of Nafion-117 membrane and IPMC is analyzed which gives the value of yield strength, elongation, ultimate strength and young modulus. Tensile testing is done by following ASTM-D638 standards. The life of ionic polymer metal composite depends on the tensile strength because, during cation migration in IPMC, elongation takes place. The value of various stress obtained after tensile testing is given in the table-1.

3.4.1 Results of tensile testing

From tensile testing following results were obtained-

(a) The breaking stress and yield strength of IPMC is more than the Nafion-117 membrane
(b) The fracture in the Nafion-117 membrane occurs suddenly.
(c) The overall elongation in Nafion-117 membrane is more.

Table 1: Results obtained after tensiletesting

S, No.	*Values*	*Nafion-117*	*IPMC*
1.	Maximum Stress	12.52 MPa	23.52 MPa
2.	Elongation at break	87%	49%
3.	Strength	3.94 MPa	7.42 Mpa
4.	Young Modulus	49.12 MPa	122.79 Mpa

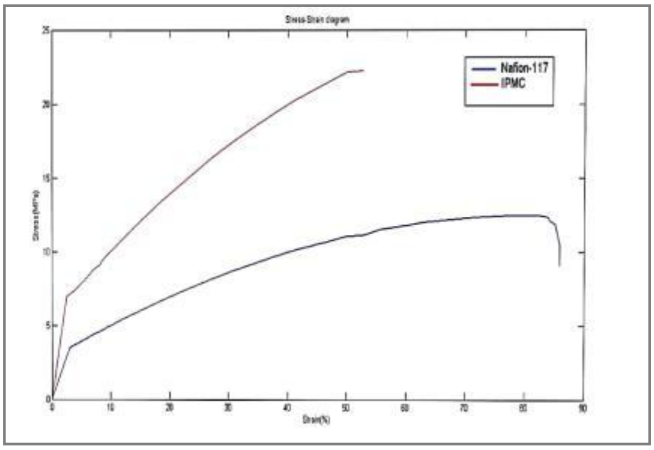

Figure 6: Stress-strain Diagram of Nafion membrane and IPMC

3.5 Surface Morphology of IPMC

The surface morphology of Nafion membrane and ionic polymer metal composite is determined by SEM- scanning electron microscope testing. The samples are prepared to withstand vaccum condition and high energy beam of electron. Samples are generally mounted rigidly to specimen holder using a conductive adhesive. For IPMC surface morphology SEM (TESCAN-MIRA 3LMH) surface topographical structure with an accelerating voltage of 5.0 kV are taken.

The images obtained from SEM testing indicate that there is proper adhesion between Nafion, Titanium and Gold metal layer. The electrode surfaces are deposited uniformly.

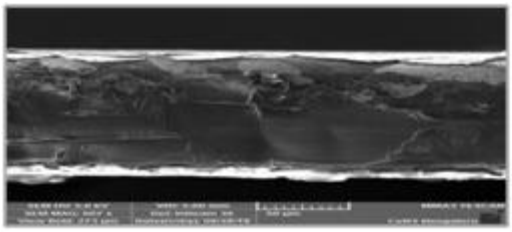
Figure 7 (a): SEM Images after Deposition

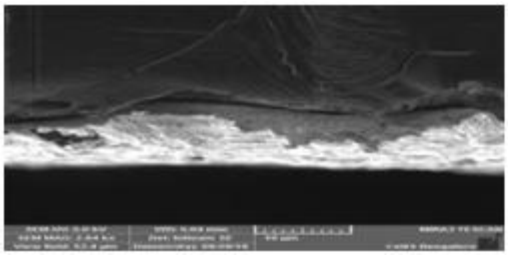
Figure 7 (b): SEM Images after Deposition

4. Application

The IPMC is having the capability of responding in a humid environment. IPMC is subjected to change in capacitance or resistance when there is moisture content therefore in this work basic humidity sensor is developed which justifies the use of IPMC as a humidity sensor. The development of low-cost humidity measurements is essential for application in the environmental, agricultural, medical and industrial fields.

The basic principle of IPMC based humidity sensor is that when moisture content increases a resistance of IPMC decreases. This happens because of the faster movement of cations as variation in moisture content.

4.1 Experimentation

For understanding the basic development of IPMC as humidity sensor experiment is done and change in output variable corresponding to change in the input variable measured.

4.1.1 Procedure

For measuring change in resistance values corresponding to relative humidity (RH) change firstly, The closed Container is dried properly with drier, then Hot beaker with steam is placed inside the container. Hygrometer is also placed over hot beaker. IPMC sample with fixture put inside the container, Then after leaving the container for 10 minute Observe the hygrometer and note the value of RH and also Observe the multimeter and note the value of resistance.

Simultaneously note the time required for resistance value to be constant from fluctuating value state stopwatch. Again leave the system for 10 minutes and repeat the steps which are mentioned above for 5-6 readings.

Figure 8: Experimental Set-Up

4.2 Observation Table

Table 2: Observed Values for IPMC Sample

S.No.	*RH (%)*	*Resistance (MΩ)*	*Response Time (sec)*
1.	10	9.01	70
2.	20	8.53	68
3.	30	7.32	65
4.	40	6.66	69
5.	50	5.46	62
6.	60	4.82	59
7.	70	3.725	56
8.	80	2.626	55
9.	90	1.875	53

The table 2 shown above consist response time (time after which multimeter shows constant value of resistance) and resistance value with varying relative humidity condition.

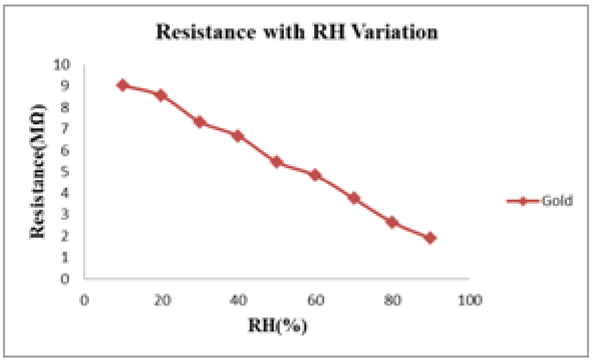

Figure 9: Resistance with RH variation in IPMC (Gold Coated)

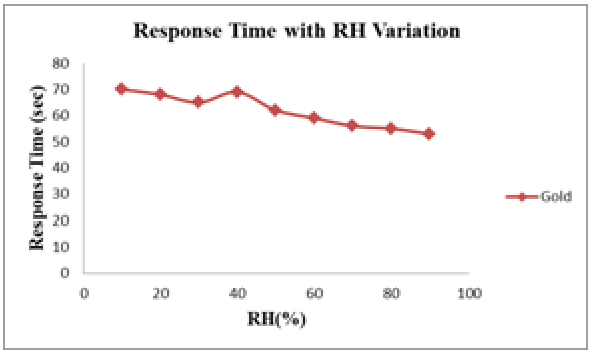

Figure 10: Response Time with RH variation in IPMC (Gold Coated)

Sensitivity is important characteristics for determining the performance of any sensor. If there is huge change in output value corresponding to small change in input value, this give potential that given system is suitable to use as a sensor. Basic formula for calculation of sensitivity value is given as:

$s = \frac{\Delta R}{\Delta RH}$ (1)

S= Sensitivity of Humidity Sensor

$\Delta R = \frac{R - R_{90}}{R_{90}} \times 100$ (2)

R= Resistance at particular value of RH

R_{90}= Resistance at 90% RH

$\Delta RH = RH - 90$ (3)

R_{90} is taken as reference value for calculating sensitivity value at different RH values.

4.3.1 Senstivity Values

Table 3: Sensitivity **at different RH**

S.No.	*RH (%)*	*S (RH%)-1*
1.	10	4.756
2.	20	5.07
3.	30	5.27
4.	40	5.104
5.	50	4.78
6.	60	5.235
7.	70	4.93
8.	80	4.012

The average value of sensitivity for Gold IPMC based humidity sensor is **4.895.**

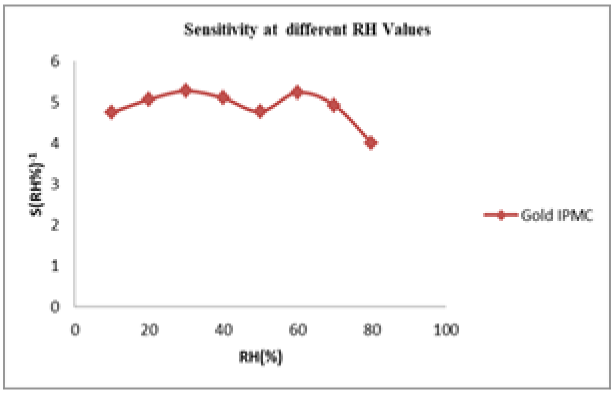

Figure 11: Sensitivity with RH variation

5. Conclusions

The physical vapour deposition method which is described above gives the uniformly deposited electrodes over IPMC. The SEM surface morphology images show the uniformity in a deposition. The stress-strain curve shows after deposition of electrodes strength of IPMC increases which indicates towards durability of fabricated IPMC when used as transducers. In this method, the desired amount of thickness can be obtained which is not possible with some another fabrication method. This method is economical for the same amount of thickness as well as less time consuming, but dehydration of electrodes takes place with time which reduces its life.

The Sensitivity values of IPMC based humidity sensor indicates that IPMC has potential to use as a humidity sensor. the only limitation is that the response time of this sensor is more.

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