國立交通大學

機械工程學系

碩士論文 基於電致動離子聚合物之人工肌肉驅動器研究 Fabrication and Actuation of Linear Contraction Type Electro-Active Ionic Polymer Metal Composite Actuator

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基於電致動離子聚合物之人工肌肉驅動器研究

Fabrication and Actuation of Linear Contraction Type Electro-Active Ionic Polymer Metal Composite Actuator

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Mechanical Engineering

July 2010

Hsinchu, Taiwan, Republic of China

中華民國九十九年七月

藉由應用電致動離子聚合物,有很多新奇的機械裝置的原型已經被開發出來了。例如:仿 生機器魚、仿生翅膀、膠囊形態的內視鏡、人工尿導管、雙穩態的自動切換開關。在大 部份的應用之中,電致動離子聚合物都是呈現一種彎曲的運動形態。即便是被做成線性 的致動器,本質上也仍然是利用串聯的方式達成線性移動。電致動離子聚合物所製成的 致動器有一個共通的限制:輸出力很小。研究顯示,增加厚度似乎是一種有效的增加輸出 力量的方法。一般電致動離子聚合物薄膜的厚度大約是 0.2mm 至 0.3mm,而且 4cm 長 的樣品的末端輸出力一般都小於 10gf。而對於一個同樣長度,但是厚度達 2mm 的樣品, 末端輸出大約是 20gf。雖然力量的增加很明顯,但是製作這樣厚度的樣品不僅費時,而 且成本高昂。在本研究中將會嘗試一種利用電致動離子聚合物所製成的近似線性的新型 致動器。同時也設計了一種節省材料的種厚極窄電致動離子聚合物,並且和一般較薄的 電致動離子聚合物做比較。實驗結果顯示,新型的致動器雖然可以運作,但是並沒有如 預期般表現出線性致動的效果。不過此種極窄極厚的電致動離子聚合物確實是一種可以 利用少量材料來製造出極厚電致動離子聚合物的設計。

Abstract

Many novel applications of Ionic polymer-metal composite (IPMC) had been developed, such as biomimetic robotic fish and wing-like actuators, capsule-type endoscope, artificial urethral sphincter, self-switching bistable actuator, etc. For almost applications, the movement type of IPMC is in bending direction. Even though the linear actuators based on IPMC are also composed of the series connection of IPMC strips. Therefore, the linear actuation of IPMC is still bending type actuators in essence. The apparatus of IPMC have the common limitation: the lack of output force. Currently, increasing the thickness of IPMC strips seems to be an effective method to reinforce the bending force. The typical thickness of an IPMC strip is about 0.2 to 0.3 mm, and the tip force is usually less than 10 gf for the length of 4 cm. And the tip force for a 2 mm thickness IPMC strip could be reached about 20 gf. Although the increasing of force is significant, but it is expensive and requires much work and time to fabricate a specimen. In this project, an approximate linear contraction type IPMC actuator is discussed. In this project, a very thick and very narrow IPMC is introduced. And this kind of IPMC is a material saving design. According to the experiment result, the very thick and very narrow IPMC worked. But the motion type of the IPMC did not the linear type as predicted. However, this material saving design is an effective way to make a very thick IPMC by using a small amount material.

誌 謝

兩年的時間一轉眼就過去了,在這一段不長也不短的時間裡,面臨了不少挑戰,不 論是修課或是研究,亦或是日常生活和感情方面的問題,都非常感謝週遭師長、同學、 朋友、以及家人的幫助與支持。

關於研究的題目,很多人聽到都覺得很有意思、非常奇特。但是因為跨了不小的化 學領域,所以光是在實驗的基礎方面就遇到了不小的挑戰,但是我的指導教授鄭泗東博 士給予我的鼓勵以及與老師的討論都給了我很大的幫助,最後不僅在一些研究的關鍵有 所突破,也有了自己創新獨到的地方,雖然結果並不如預期,但是能夠把構想的東西實 際做出來是一種難得的經驗,也算是對於學術有一點小小的貢獻。

另外也要特別感謝呂宗熙教授以及陳宗麟教授的指導,不管是論文內容的校核,或 是提出可供討論的意見,都使得研究的結果更趨完備。

碩士生涯即將劃下真正的句點,也代表即將脫離學生的身份,非常感謝從大學以來 一直到研究所這六年來幫助過我的同學以及朋友。感謝同實驗室的林育丞同學、吳敏瑞 同學、林志鴻同學、黃冠豪同學、胡介璿同學、傅俊傑同學、曾于恬同學、江國維學弟、 宋志豪學弟、黃靖哲學弟、曾炫錡學弟、周信宏學長、周伯謙學長,還有已經畢業的李 其韋學長、鄧義銘學長、江柏融學長、傅祥志學長。還有其他實驗室的駱炳江同學、王 炫和同學、林伯儒同學、謝一全學長、江鎮宇同學、鍾政涵同學、陳俊宏同學、施境瑋 同學、蔡正一同學、葉人瑜同學、何昇融同學、吳欣恬同學,以及齒輪實驗室的陳冠宇 博士,應用化學研究所的邱昶禎同學,還有機械系辦的劉克正先生與陳文欽先生。不論 是實驗的協助或是精神上的支持,我都由衷感謝。

最後要感謝我的父母、哥哥,雖然他們不是很清楚我的研究是什麼,但是總是很有 耐心地聽我講述研究方面的事物,也時常給我鼓勵,讓我有信心一直努力下去,最後取 得碩士學位。

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I. INTRODUCTION

1.1 Fundamental Concepts

We are able to act because we have muscle, and also due to the coordinated movement of muscles and bones. About ten years ago, the National Aeronautics and Space Administration (NASA) started to develop a series of unusual and novel robotic arms [1], [2]. In order to accomplish the sufficiently precise actions that couldn't be achieved by the traditional oil and pneumatic robotic arms. By imitating the action of real muscle of human arms, the scientists started to develop artificial muscle for the purpose. Artificial muscle is a kind of special and interesting actuator. Because artificial muscle seems to be an actuator to make machines works like a creature. So, it specially suits to be used for biomimetic robot applications. Furthermore, for some medical instrument such like bending micro-machine of catheter [3], capsule-type endoscope [4], prosthetic eye correction[5], artificial limbs, and etc. And also for machines of camera lens focusing, water or gas micro-pumps [6], micro-tweezers [7], etc. Obviously, artificial muscle has great potential to be applied in many fields. Anyone can come up with a lot of ideas. But not everyone understands well that like an export. Although we may have many ideas, but the restrictions of materials don't allow us to achieve our goal. In fact, there are many types of artificial muscles made with various materials and principles. Such as, chemically activated polymers, light activated polymers, shape-memory polymers, pneumatic artificial muscles (PAMs, also called McKibben muscle), magnetically activated polymers, thermally activated gels, muscle wire, and electroactive polymers (EAPs). Nevertheless, many of them do not have practically usable performance. Some of them are too heavy to use, or the chemical reaction is irreversible so it only can shrink but can't do opposite action. So, many types of artificial muscles are just only for researching not for really useful applications. To make reality use of artificial muscle, the

material should be able to be repeatedly operated for many times. Easy to be actuated is also a very critical prerequisite to develop a device that close everyday life.

1.2 An Overview of EAPs

Electroactive polymers (EAPs) are a category of polymers that represent deformation in response to electrical signals. Furthermore, according to the actuation theory of the electroactive polymers, EAPs can be classified into two types: Electronic EAPs and Ionic EAPs [8]. Electronic EAPs are the types, which are stimulated by electric field and static electricity force that cause electronic EAPs to deform. And ionic EAPs are actuated due to the polymers that contain the corresponding ions. When the electric field is applied to the ionic EAPs, the ions in the polymers start to move. The direction, that ions move to, is base on the ions are cations or anions, and the direction of electric field is also important. Several kinds of EAPs are shown in the Table 1.1. Several EAPs are introduced below.

E	E E
Electronic EAP 189	Ionic EAP
Dielectric EAP	Ionic polymer gels (IPG)
Electrostrictive graft elastomers	Ionic polymer metal composite (IPMC)
Electrostrictive paper	Conducting polymers (CP)
Electro-viscoelastic elastomers	Carbon nanotubes (CNT)
Ferroelectric polymers	
Liquid crystal elastomers (LCE)	
Carbon nanotube aerogel sheet	

Table 1.1 several types of electroactive polymers

1.3 Dielectric EAP

The material used to make dielectric EAP is very elastic and the total volume of the material almost wouldn't change when dielectric EAP is actuated [8],[9],[10],[11]. According to Coulomb's law, when a pair of parallel metal plates to be applied an electric field on it, the electric charges on the metal plates would cause electrostatic force. The electrostatic force would narrow the distance between the two metal plates. The dielectric EAPs are made by inserting the elastic material into the gap between the two metal plates. The netal plates. The netal plates. The dielectric field to be applied on the parallel metal plates. As a result, the medium material became thin and flat and also enlarged horizontally. The illustration diagram is shown in Figure 1.1 and Figure





Figure 1.1 initial state of dielectric EAP



Figure 1.2 actuated dielectric EAP

The contrast operation is to disconnect the electricity source and let the two metal electrodes to be short-circuited. The charges accumulated on the electrodes would flow to the opposite electrode through the wire. The electrostatic force disappeared, and the medium went back to initial shape.

1.4 Ferroelectric Polymers

Ferroelectric materials are usually made with poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE))[12], [13]. The electric field be applied on the ferroelectric materials causes aligning of the local dipoles, which locate on the backbone of the polymer, as shown in figure 1.3 and figure 1.4.



Figure 1.3 canceling dipoles (nonpolar)



Figure 1.4 additive dipoles (polar)

So, the electric field aligned the local dipoles and the local dipoles generated the local polarized domain. Just like common Ferro-magnets, some of the polarization of the dipoles may exist permanently even the electric field to be removed. And the destruction of the polarization may occur when the temperature of the material to be raised to the particular Curie temperature. The reversible structural transform induced by the polarization of the dipoles in the polymers have the potential to be used as an actuator.

1.5 Liquid Crystal Elastomers

Liquid crystal elastomers (LCEs) can be actuated by applying joule heating on the polymer [14], [15]. Liquid crystal elastomers are composite materials. They are made of nematic liquid crystal elastomers with uniaxial or biaxial mesophase having one or two directors. And LCEs have conductive polymers to be distributed into its molecule structure. The alignment and order change of the liquid-crystalline side chains generates stresses in LCEs, and the stresses cause the actuation of LCEs. Thermal and electrostatic energy can be used to change the alignment of the liquid-crystalline side chains. For common liquid crystals, stress fields cause the flow of the polymers so the stress won't be accumulated to generate static forces. But in the LCEs, the liquid crystal polymers are embedded into cross-linked molecule structure backbones. The elastic polymer backbones block the flow of the liquid crystals, but it permit the liquid crystals to change alignment direction. So, the static force wouldn't be released.



Figure 1.5 chemical structure of a side-on LC monomer



Figure 1.6 schematic of the side-on LC elastomer structure

1.6 Carbon Nanotubes

Carbon nanotube was introduced as a new actuator material in 1999. The carbon nanotube actuators are usually made of single-walled carbon nanotubes [16]. Single-walled carbon nanotubes can induce higher stresses than real muscles. The carbon nanotube actuators have a similar feature to nature muscles, the actuators are combined with many microscopic actuators. And the force generated by the microscopic actuators can be accumulated to cause a macroscopic deformation. To actuate the carbon nanotube actuators, the actuator should be immersed in an electrolyte first. Then inject charges into the single-walled carbon nanotubes, as shown in figure 1.7.



Figure 1.7 the concept of the injection of single-walled carbon nano tubes

If the carbon nanotubes are injected in negative charges, the nanotubes would be surrounded by cations and positive charges would contrary make nanotubes be surrounded by anions. In order to the leaving of electrons, the carbon atoms are positively charged. And the length of C-C bonds decrease due to the quantum chemical effects. For example, an carbon nanotube actuator consists of two strips of single-walled carbon nanotubes, and the carbon nanotube actuator was immersed in NaCl solution. When charges be injected in the carbon nanotubes, the Cl^- ion attracted by the positive charge-injected carbon nanotube. The carbon nanotube surrounded by Cl^- ion would contract and the carbon nanotube surrounded by Na^+ ion would elongate, as shown in

figure 1.8.



Figure 1.8 Schematic edge view of a cantilever-based actuator.

1.7 Ionic polymer metal composite

Ionic polymer metal composite (IPMC) is a flexible material that made of ion-exchange membrane and metal electrodes[17], [18]. From almost 15 years ago, IPMC started to be researched extensively. The ion-exchange membrane most to be used is Nafion[®] 117 [19][18]. Nafion[®] 117 is a kind of perfluorinated, sulfonate membrane used to make into fuel cell membrane electrode assembly (MEA). There are several methods to be used to

coat the electrodes on membranes, such as, evaporation, sputtering, and electroless coating [20]. The most often to be used method is electroless coating, because the adhesion between the electrodes and ion-exchange membrane is usually better than the other method. If a voltage applied on the electrodes, the ion density in the membrane would be changed. Then, the change of ion density induces the deformation of the membrane, and the composite material is actuated. The detailed description would further introduced later.



II. INVESTIGATION IN IONIC POLYMER METAL COMPOSITE (IPMC)

2.1 The Basic Concepts of IPMC

IPMC (Ionic Polymer-Metal Composites) is a kind of special material. The basic structure of IPMC is composed of a piece of ion-exchange membrane with two metal electrodes coated on the two main surfaces. Applying a voltage difference on the two electrodes then the IPMC will bend toward to the higher electric potential direction [18]. As shown in figure 2.1 and figure 2.2.



Figure 2.1 Basic structure and basic actuate method of IPMC.



Figure 2.2 Actuated IPMC strip.

The movement type of IPMC is very different from traditional actuators, for instance, motor, oil and pneumatic actuator, and etc. And the bending deformation is very large with respect to piezoelectric actuators, but the voltage difference required to actuate IPMC is very small relative to which piezoelectric actuators need. IPMC just need to use several common batteries. Water molecule is a kind of polar molecule. So the water molecule in the ion-exchange membrane will combine with the cations that also included in the ion exchange membrane, and the hydrated positive ions (composed of cation and water molecule) will flow to the lower electric potential direction. That causes the higher electric potential side to contract and the lower electric potential side to swell due to the ion diffusion. Then the IPMC perform the bending deformation, as shown in figure 2.3.



Figure 2.3 The Ion Diffusion in IPMC Strips.

2.2 The Ion-Exchange Polymers

Ion-exchange polymers are materials used to be the basis of IPMC. The ion-exchange polymers have the capability to exchange ions with surrounding environment. The polymers have complex surface micro structure. There are many pores with special charge distribution on the surface of the polymers, so the polymers can trap or release ions. And when the polymer catches an ion, the polymer has to release an ion simultaneously. So, if ion-exchange polymers were immersed into an electrolyte solution. The polymer would exchange the ions that initially in the polymer with the ions that in the electrolyte solution. Ion-exchange polymers are applied to exchange ions selectively, in order to achieve specific purposes, such as water softening, water purification, producing high purity water, sugar manufacturing, and medicine purification, and etc. Ion-exchange membranes are typically produced using the polymer that has covalent ionic groups in the molecule structure. Many types of ion-exchange polymer are manufactured to specifically pick out one or several various kinds of ions. One of the common ion-exchange polymers is perfluorinated alkene. That kind of polymer has short side-chains and ionic groups at the termination of the side-chains. The ionic groups are usually sulfonate or carboxylate, and the capabilities of the ionic groups are exchanging cations and interact with water. This kind of ion-exchange material has the structure that the mechanical strength is highly depending on the network of the polymer backbones. Therefore, the variables that effect the forming of the polymer backbones are very important when fabricating polymer. The other kind of common ion-exchange polymers is styrene/divinylbenzene-based polymers. The ratio of styrene to divinylbenzene is an important factor. The factor effects the made-up polymers in the ion-exchange capabilities, crosslinking structure in the polymer, and the water absorption. The ionic groups in the cation-exchange polymers are typically sulfonate. The known effective manufacturing method to fabricate sulfonated ion-exchange membranes was on the basis of grounding the ion-exchange resins into micro-scale powders. Then mix the powders with the specific material, that the material is hydrophobic thermoplastic and include polyethylene or polyvinylidinefluoride, and press flat the mixture. Subsequently, put the mixture into an oven and give them a series heating process [18]. Lately, the paste method became an ordinary and well-known method. The feature of the method is a hydrophobic polymer. The paste that includes the liquid phase monomers is mixed with the minute particle of hydrophobic polymer. The initial mixture and the plasticizer usually control the outcome of the polymer [21].

2.3 Nafion[®] Membrane

Currently, the most commonly used commercial ion-exchange polymer is Nafion[®]. Nafion[®] is a product of DuPont[™]. Nafion was be discovered by Walther Grot in the 1960s. Nafion[®] is a kind of fluoropolymer-copolymer bases upon sulfonated tetrafluoroethylene (Teflon). The special ionic characters of Nafion[®] are result in the molecule groups that embedded onto tetrafluoroethylene backbones. The critical molecule groups are incorporating perfluorovinyl ether groups and the molecule groups have sulfonate groups connect with terminals of the incorporating perfluorovinyl ether groups. Many researchers paying attention on Nafion[®] membrane, because Nafion[®] membrane can be used to be a very important component for proton exchange membrane (PEM) fuel cells. Nafion[®] membrane is as a key role in proton conductor. The Nafion[®] membrane is widely used owing to the thermal and mechanical stability of Nafion[®] membrane is very remarkable [22]. The molecule formula is shown in Figure 2.3.



Figure 2.4 Nafion® polymer molecule structure

The excellent ion conductive characters of Nafion[®] polymer is still a focal point of investigation. The sulfonic acid groups have protons on itself, and the protons on the groups can bounce to the other sulfonic acid groups from the initial group. The pores on the Nafion[®] polymer permit cations to migrate in the polymer, but the polymers don't allow anions or electrons to transfer. The protons or the other cations initially in the Nafion[®] polymer can be replaced with several kinds of cations of conductors. The

property of Nafion[®] membrane could also be changed through the process. Nafion[®] powders and copolymer are available products through appropriate manufacturing method. Nafion[®] polymer has not the only one chemical name in the International Union of Pure and Applied Chemistry (IUPAC) system. Because of the chemical configurations of Nafion[®] is not only one type, too. The molecular weight is also indeterminate owing to divergences of fabricating process and morphology of solution. Traditional measurement means such as, light scattering and gel permeation chromatography are useless for Nafion[®] polymer, because Nafion[®] polymer is unquestionably insoluble. Even though the molecular weight of common Nafion[®] polymer has been estimated, it's about 105-106 Da. Furthermore, the other way to describe the common commercial Nafion[®] product is the equivalent weight (EW) and the thickness of the membrane. Equivalent weight concerns the total amount of sulfonic acid group that is included in the Nafion[®] membrane. The definition of EW is the weight of Nafion[®] membrane that has total one mole of sulfonic acid group in the membrane. For instance, the EW of Nafion[®] 117 is about 1150, and the thickness is about 183micrometer. The main factors effect the properties of Nafion® are the stable tetrafluoroethylene backbone and the acidic sulfonic groups. For example, the conductivity of cations in the membrane is excellent, so the Nafion[®] membrane is used in many applications that need selectively transparent of specific ions. And the stable property due to the tetrafluoroethylene backbone gives Nafion[®] the capability to be operated in high temperature. But, one important phenomena should be careful about. That is, although the Nafion[®] polymer is good in the permittivity of water, but if there were too many water molecules in the membrane, the transmission of ions would be disturbed. For the operation of PEM fuel cells, the property should be concerned carefully, because the byproduct of the PEM fuel cells is just water.

The properties of Nafion[®] polymer are important, and of course the actual structure of Nafion[®] polymer is also very important. The study in the morphology of Nafion[®]

membranes is a focal point to further understand the property and operation of Nafion[®] membrane. Some properties must be illustrated by the research of the structure, such as the management of water in the membrane, the high temperature condition that affects the hydration stability, etc. And the most important, the electro-osmotic drag. It might be the direct factor concern the property of IPMC. Electro-osmotic drag is the phenomena that the liquid with polar property flow through a thin membrane or a material that has many porous in the structure due to the electro field that is applied on the material. And the polar liquid may also flow along the surfaces of any shape that had been charged. Not only macro-porous material can allow polar liquid to flow through by, the micro-porous or even the nano-porous materials, that include ionic trapping sites and permit the absorption of water, also allow the transport of polar liquid. In the field of electrochemistry, physics and vascular plant biology, electro-osmosis has another name: electroendosmosis. Electro-osmosis was discovered by F.F. Reuss first in 1809, and now has several applications in the field of microfluidics and PEM fuel cells. The first structure model of Nafion[®] polymer is composed of sulfonate ion micelles that distribute uniformly in the polymer structure, and the model is called the Cluster-Network Model or called the Cluster-Channel. Micelle is a kind of special molecule structure. The aggregation of surfactant molecules that suspend in a liquid colloid could be a spherical construction. The spherical construction often consist of hydrophilic head regions on the spherical surface that contact with liquid, and the hydrophobic tail regions are isolated in the center of micelles. But the micelles of Cluster-Network Model are called the inverted micelles. Because the position of hydrophilic head regions and the hydrophobic tail regions of Nafion[®] molecule in the micelles are reversed. So, the center of the micelles permits the transmission of water and ions. A continuous fluorocarbon lattice held the micelles in the fixed positions. The clusters are about 40 Å in diameter and the channels have the diameter about 10 Å interconnect the micelles [23]. The concepts are illustrated

in the figure 2.4, and figure 2.5.



Figure 2.5 Structure of spherical micelle.



Figure 2.6 Cluster-network model for the morphology of hydrated Nafion[®] polymer.

The diversified derivatives of Nafion[®] polymer cause the two major problems that increase the difficulties in determining the actual polymer structure of Nafion[®] membrane. The two problems are the uncertainty of the solubility and the inconsistent crystalline structure. The other Nafion[®] advanced morphological models were also proposed. The categories have included a core-shell model, a rod model, and a sandwich model. The core-shell model is considered as the Nafion[®] polymer structure separates into two parts: ion-rich region and ion-poor region, and the ion-rich regions are the cores surrounded by

the ion-poor shells [24]. The rod model describes the structure that the arrangement of sulfonic groups in the Nafion[®] membrane is the crystal-like rods. The third model is the sandwich model, the middle of the model is an aqueous layer where the water and ion transport occur, and the two layers on both sides are composed of sulfonic groups where the sulfonic groups attract each other across the middle aqueous layer. The models are different from each other, because the cluster geometry and the cluster distribution. Even though the models are not really match the actual structure very well. A demonstration has been announced by some scientists. The demonstration says that because the Nafion[®] polymer is a kind of membrane hydrates, the morphology of Nafion[®] polymer could be the cluster-channel model and then transfers to the rod-like model. The diagram of the models are shown in figure 2.6, figure 2.7, figure 2.8.



Figure 2.7 Separation of hydrophobic fluoro-carbon backbone polymer and hydrophilic side-chains.



Figure 2.8 Structure element with sandwich structure.



Figure 2.9 Composition of basic structure elements to complex channel structures.

Another recent structure model theory is the water channel model. Combine the simulation result, that according to the data of small-angle X-ray scattering [24], as shown in figure 2.9, and the observation result of solid state nuclear magnetic resonance [25].



Figure 2.10 Schematic experimental set-ups for in situ measurements with synchrotron

The conclusion is the water channel model. The concept is illustrated in figure 2.10.



Figure 2.11 Two views of an inverted-micelle cylinder, with the polymer backbones on the outside and the ionic side groups lining the water channel.

This model gives several individual descriptions of Nafion[®] polymer structure. First, the hydrophilic water channel is composed of sulfonic acid functional groups, and the construction of the channel is by the self-organization phenomenon of sulfonic acid functional groups. Second, the hydrophilic water channels are about 2.5 nm in the diameter, and the hydrophilic water channels could let the ions efficiently transport through. Third, the polymer backbone construct from hydrophobic polymer includes crystallites, and the quality of the backbone affects the stability of mechanical of membrane. The water channels are parallel to each other and the several crystallites also distribute in the construction. The hydrophilic sulfonic acid functional water/ion channels, hydrophobic fluoro-carbon backbone, and crystallites construct the structure of Nafion[®] polymer as shown in figure 2.11[25].



Figure 2.12 Diagram of the approximately hexagonal packing of several inverted-micelle cylinders.

2.4 Casting Method of Nafion[®] Membrane Fabrication

The Nafion[®] membrane is the key component of IPMC as said above. Before making the IPMC strips, the Nafion[®] membrane should be prepared first. But the manufacturing of Nafion[®] membrane is not an easy work. Many variables influence the final product of Nafion[®] membrane, such as the bubbles in the Nafion[®] dispersion during the baking, the heating process, the mold that contain the Nafion[®] dispersion, etc. Nafion[®] dispersion and Nafion[®] membrane are commercial available material. But the Nafion[®] membrane just has only few specifications. If the experiment needs thicker membrane, to fabricate a custom membrane is the only way. The basic fabrication of Nafion[®] membrane needs several critical apparatus, as shown in the table 2.1.

Apparatus	Application
vacuum oven	To bake the Nafion [®] dispersion
molds	To contain the Nafion [®] dispersion

Table 2.1 the basic equipments that to be used to fabricate Nafion® membrane

The manufacturing of Nafion[®] membrane is step by step. The first step is the mold design. The shape of mold is arbitrary. But the volume of mold should be carefully calculated. The dispersion contains many organic solvent and water, and the Nafion[®] polymer in the dispersion is only less than 20%. Most of the dispersion would evaporate during the baking. Although the baking process can be operate repeatedly, but it waste time and works. For instance, if the product number is "D 520" the dispersion contains 5% Nafion[®] polymer [26]. The unit of 5% is the weight of Nafion[®] polymer per 100 gram the dispersion. Next, the specific gravity of the 5% Nafion[®] dispersion is about 0.92 – 0.94 (*g/mL*). And the specific gravity of the Nafion[®] membrane is about 1.98 (*g/mL*). So, the volume of Nafion[®] membrane per milliliter is able to be calculated. The calculation is shown in equation (1).

$$1(mL) \times 0.94(g/mL) \times 5.0\%(wt.\%) \times \frac{1}{1.98(g/mL)} = 0.0247(mL)....(2.1)$$

If the mold is a simple rectangular shape, and the area of the bottom is about 25 (cm^2). The thickness wanted is about 0.2 (mm). The total volume of dispersion required is about

$$25(cm^2) \times \frac{0.2}{10}(cm) = 0.5(cm^3)....(2.2)$$

$$\frac{0.5(cm^3)}{0.0247(mL/mL)} = 20.24(mL)...(2.3)$$

Total 20.24 (mL) Nafion[®] dispersion is required. And the height of the mold is about

$$\frac{20.24(mL)}{25(cm^2)} = 0.8096(cm)...(2.4)$$

The height of the mold is about 1 (cm). And if the thickness of Nafion[®] membrane required is 2 (mm), the height of the mold is ten time of the 0.8 (cm). The mold might have a big volume. The material used to make a mold is usually glass and acryl. The glass usually be the bottom of the mold, and the acryl is used to be the sidewall. The gap between the glass and the acryl can be filled with poly dimethyl-siloxane (PDMS). The glass transition temperature of PDMS is about 120 °C, so the conservative operation temperature of the mold is about 100 °C. The second step is pouring the dispersion into the mold. When treating the Nafion[®] dispersion, the operator should be as careful as possible, because the methanol vapor of Nafion® dispersion is deleterious to breathing system and neural system of human. You should wear eye shields, disposable gloves, type N95 or type P1 (EN143) respirator before opening the dispersion bottle. To draw the dispersion from the bottle, use a clear dropper to avoid the pollution of the dispersion in the bottle. After pouring the dispersion in the mold, putting the mold contained the dispersion into the vacuum oven. The clearance of vacuum oven chamber is very important, because the dirty particles in the dirty chamber could pollute the Nafion® dispersion. The final Nafion[®] membrane would contain impurities. The impurities would cause the failure of the Nafion[®] ion-exchange ability. The details of heating process
would be explained in the chapter of experiment.

2.5 Coating of Electrodes

The electrodes coated on Nafion[®] membrane require two important properties: the adhesion between electrodes and Nafion[®] membrane surface, and the low surface impedance. The IPMC is an actuator so the Nafion[®] membrane would deform during actuating. The electrodes coated on the two edge sides also bear the stress and strain due to the deformation of Nafion[®] membrane. Therefore, the adhesion of electrodes is important. When a voltage difference applied on the IPMC specimen, the electrical field generated between the two electrodes. And the clip usually only fixes one side of IPMC strip. If the surface impedance of electrodes were too high, the electrical field would distribute not uniformly. And the performance of IPMC strip would be influenced. To coat the effective electrodes, the steps are familiar with fabricating the Nafion[®] membrane. The coating steps are combined with the Nafion[®] membrane fabricating steps. As shown in figure 2.12 [27].



Figure 2.13 illustration of the fabricating method of electrodes

The first step is mixing the ion conducting powder (carbon, platinum, palladium, gold, copper, silver, etc) with the Nafion[®] dispersion. The powder is very tiny, and distributed in the Nafion[®] dispersion uniformly. Then pour the mixed dispersion into the mold to form a thin electrode layer, and drying the electrode layer. Second step is pouring the pure Nafion[®] dispersion on the top of the previous electrode layer, and also drying the pure Nafion[®] dispersion layer. The final step is the same to the first step.

2.6 Recent Applications of IPMC

As an electroactive material, IPMC have been widely developed for many purpose. No matter the research results are useful or unpractical, the IPMC actuators still progress. The main difficult problem of developing IPMC actuators is the weakness of IPMC. The output force of IPMC is very small. The small output force causes the problems on macro scale applications. So, many experiments had shown low movement speed, and small displacement when the actuator had a loading on it. But, there are still some meaningful researches, such as biomimetic jellyfish robot [28] and self-switching bistable actuator [29]. Jellyfish is soft and the movement type is not too complex to simulate. IPMC seems to be an excellent material suits to make the biomimetic jellyfish actuator. The researchers of Chonnam National University at Korea had made an in-depth research in biomimetic jellyfish actuator. They fabricated a kind of custom shape IPMC specimen. The IPMC specimen looks like a flattened eight lags starfish, as shown in figure 2.13.



Cellophane paper

Biomimetic jelly fish

Figure 2.14 components of biomimetic jellyfish

And then, they use cellophane paper to combine with the IPMC specimen to make a emisphere structure. The starfish-like IPMC can act like a claw, and the cellophane paper is like the web of a duck. When the IPMC specimen grabs the water in the hemisphere would be squeezed out, and the artificial jellyfish would be propelled forward. The

self-switching bistable actuator is another clever idea. IPMC strip in this experiment is treated as a flexible reed. And the deformation of the IPMC strip is considered as the bending of a reed due to the force applied on the two sides. And the force applied reed would have two stable buckle types, as shown in figure 2.14. Theoretically, there are two transition types between the two stable buckle types, as shown in figure 2.15 and figure 2.16. By controlling the deformation of IPMC strip, the choice of bending stable type can be demonstrated.



Figure 2.16 the transition type I



Figure 2.17 the transition type II

2.7 The Basic Electrical Characters of IPMC

IPMC is a sandwich structure consisting of a middle ion-exchange membrane and two thin electrode layers on the two sides. The electrical properties of IPMC can be seen as same as a

capacitance parallel connects with an equivalent resistance. The electrical properties of various capacitances are different, and the IPMC properties are usually measured by instruments. Another factor is that, IPMC strips deform when be actuated, so the electrical properties of IPMC would change during actuating. To actuate a common IPMC strip with 0.2 (mm) thick, 10 (mm) wide, and 40 (mm) long usually needs about 25 - 30 (mA) when a 2 (volt) amplitude signal applied on it. And the surface resistance would cause the voltage drop along the electrodes. The frequency response of the IPMC strips is also a variable property. The factors such as the thickness, length, counter ion, etc are influential to the properties of IPMC.



III. THE APPROXIMATE LINEAR ACTUATOR

3.1 Approximation of Linear Actuation

The IPMC actuators usually the applications of a bending type movement IPMC strips. Obviously, the IPMC specimens are also usually made into a thin and long strip form. And the IPMC specimens perform a bending deformation naturally. Even though the IPMC strips are used to compose a linear actuator, it is still an application of bending deformation, as shown in figure 3.1.



Figure 3.1 a typical IPMC linear actuator

The critical problem is not the stroke length of the actuator. In fact, the large deformation is one of the excellences of IPMC strip. The really critical problem of the actuator is the output force. The output force of a single IPMC strip is really small as said above. Although the linear actuator can be composed of strips as many as possible, that is not an efficient design. The total weight of the actuator is not light, and the volume is big relative to the other actuators that can generate same output force. The disadvantages cause the application of the actuator is impractical. To solve the problem, use thicker IPMC strips is a reasonable method. But the improvement of the linear actuator by using thicker IPMC strips is not proportional to the cost and work to make typical thicker IPMC strips. In this project, an innovative design is proposed. The structure of the approximate linear actuator is actually similar to the typical linear actuator. First, two IPMC specimens with different thickness is introduced, and the length and width are the same, as shown in figure 3.2.



The key point of the structure of the approximate linear actuator is the using of the thicker 1896 IPMC specimen.

The analysis is based on an assumption. The analysis assumes that the deformation of a small segment of an IPMC strip is an arc [30]. And the change in thickness is ignored. The illustration diagram is shown in figure 3.3.



Figure 3.3 the assumption of arc deformation

According to the assumption, the thicker strip has a larger deformation. And the comparison of the thin and thick IPMC specimens is shown in figure 3.4.



Figure 3.4 the comparison of the deformation of thin and thick IPMC specimens

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The solid and hollow dots on the rectangle corners are called the mass points. According to the mass point geometry, the displacement vectors of the mass points are very different. The displacement vectors of the thin IPMC strip are oblique, and the displacement vectors of the thick IPMC strip are almost vertical. The diagram suggests that the thicker IPMC strip can produce a more linear displacement.

If the thickness of the IPMC is wide enough, such as 3 mm wide, a small hole can be located at a corner of the IPMC. And a load can hang at the hole. When the IPMC deforms, the local linear movement of the hole can drag the load to perform a linear movement, as shown in figure 3.5.



3.2 The Improvement of IPMC Fabrication

Even though the thick IPMC specimen is an ideal material, the fabrication of thick IPMC strip is still an obstacle. The Nafion[®] dispersion and Nafion[®] membrane are expensive materials. As said above, the fabrication of a 2 (mm) Nafion[®] membrane needs about 200 (mL) Nafion[®] dispersion. The cost is about five thousand New Taiwan Dollars. In fact, the thick IPMC specimen might be fabricated in the other cheaper way, as shown in figure 3.5.



Figure 3.6 the concept of improved fabrication method

The initial concept is the change of the angle of view. The left side of the figure 4.7 is a common IPMC strip, that is only 0.2 (mm) thick and 5 (mm) wide. Then turn the strip to let it stand up, and change the position of the electrodes from the original location to the other two edge sides of the strip. A very thick IPMC specimen with 5 (mm) in thickness and only 0.2 (mm) in width is accomplished. Actually, the method might not work. Because the water channel of ion-exchange may be a parallel arrangement. And the water channels are perpendicular to the surface of ion-exchange membrane, as said at previous chapter. So the actual fabrication method is not just turn the direction of the ion-exchange membrane. The method would be discussed in the chapter of experiment.

3.3 The Simulation of Bending Motion

The simulation of the bending motion of IPMC strip with different thickness is according to the equation shown below [30]. And the result is shown in Figure 3.6.

$$\kappa_{E} = \left(\frac{1}{2 \cdot Y \cdot C^{*}}\right) \left\{ R \cdot T \cdot \left[2 \cdot C_{g} \cdot V \cdot \frac{\left[1 - e^{\frac{-t}{R_{g}C_{g}}}\right]}{n^{*} \cdot e \cdot A_{v} \cdot \left(l_{g} \cdot w_{g} \cdot t_{g}\right)} \right] + 2 \prod_{hw} \right\}.$$
(3.1)



Figure 3.7 The simulation result of different thickness IPMC strips.

From the simulation result, the curvature of IPMC strips is inversely proportional to the thickness. And the result implies the linear type actuation of thick IPMC.

IV. PREPARATION OF ION EXCHANGE MEMBRANE

4.1 The Choice of Ion Exchange Resin

The main component of ionic polymer metal composite (IPMC) strip is ion exchange resin. There are several kinds of ion exchange resin could be chosen to make IPMC [17]. As shown in table 4.1.

Company	Product(s)
DuPont [®]	Nafion [®]
Tokuyama [®]	Neosepta®
Asahi Chemical [®]	Aciplex [®]
Asahi Glass [®]	Flemion [®] ; elemion [®]

Table 4.1 several kinds of ion exchange resin provided by different company

The Nafion[®], product of DuPont[®], is a kind of common commercial ion exchange resin. In this project, Nafion[®] is chosen to compose IPMC strips. Because of the convenience of acquiring the material and most of the papers reported the choice of same material. The Nafion[®] dispersion and membrane that directly bought from commercial agent are both applied in the experiment of this project.

4.2 The Process of Making Nafion® Membrane

To make a Nafion[®] membrane from Nafion[®] dispersion, the first step is to make a mold. The mold is used to contain the Nafion[®] dispersion, and the shape of the mold is arbitrary. The height of the mold should be calculated during the process of mold design. The second step is pouring the Nafion[®] dispersion into the mold. The process of pouring the dispersion can be accomplished easily by using a common plastic 5mL dropper. And the quantity of Nafion[®] dispersion could be calculated at first. According to the Chapter 2.4, the computing needs to

know the mass density of the Nafion[®] dispersion and Nafion[®] membrane, mass percentage of Nafion[®] dispersion, the bottom area of the mold, and the thickness of the final product. Furthermore, the volatile component of the Nafion[®] dispersion is a little harmful to human respiratory organs and neural system, to wear a P95 respirator during the operation is recommend. The third step is letting the Nafion[®] dispersion dry at atmosphere. During the drying process, the dust should be kept out of the mold. The drying speed is due to the quantity of Nafion[®] dispersion and the atmosphere circumstances, such as humidity, temperature, and the airflow in the room. In fact, the drying process is separated into several steps. The Nafion[®] membrane would split easily due to the shrinkage during the drying process. Because, the shrinkage would induce internal stress that cause the breaking of the membrane. To fix the breaking on the membrane, the second time pouring should be executed after the membrane dried first time. The required quantity of Nafion[®] dispersion is just to submerge the dried membrane in the mold. After the second time drying, the membrane should totally separate from the wall of the mold. If the membrane is still broken, the third time pouring should be executed. The third step is finished until the membrane is formed into a unity. Then the forth step is the heating process. The main purpose of heating process is to change the characteristic of the membrane. If a Nafion[®] membrane is produced by evaporation of Nafion[®] dispersion at room temperature, the fluorocarbon molecule chains are dispersed. This kind of Nafion[®] membrane would be dissolved again by alcohol and water. And the mechanical strength of the membrane is very weak. In order to prevent the situation occur, the Nafion[®] membrane should be heated to about 160 $^{\circ}$ C [31]. The fluorocarbon molecules in the membrane will extend and fuse together. After the heating process, the mechanical strength of the membrane will increase, and the membrane will become insoluble. The final step is putting the Nafion[®] film into ionic solution, such as sodium hydroxide (NaOH) solution, lithium hydroxide (LiOH). The purpose of final step is to exchange the original H^+ (proton) in the Nafion[®] film with the ions in the ionic solution. And the ion



exchange process is optional. The flow chart is shown in figure 5.1.

Figure 4.1 the flow chart of heating process

4.3 The Different Kinds of Molds

In the experiment, many kinds of ideas are tried. And there are several varieties of mold. The first type mold is acrylic mold. It was made of acryl and glass. Acryl was made into the wall of the mold, and the glass was used to be the bottom plate. The acryl was glued to glass plate with polydimethylsiloxane (PDMS). The design is briefly shown in figure 4.2 and figure 4.3. And the photo is shown in figure 4.4.



Figure 4.2 the oblique drawing of first type acrylic mold



Figure 4.4 the photo of the acrylic mold

But the mold had a problem. During the milling work of acrylic component, the milling cutter would produce heat at the cutting position. And the heat would cause the deformation of acrylic material. So the bottom of the acrylic mold wall is a little curvy. The gap between the acryl and glass plate caused some pattern on the bonding area. But that had no influence on the air tightness of the mold. The picture is shown in figure 4.5.



Figure 4.5 the photo of the pattern

The second type mold was totally made of glass. Because of the manufacturing process is more convenient than first type. The curve phenomenon of acryl was also improved. The difference between first type and second type mold is the material of the wall of mold. The wall of the second type mold is made of glass slide($25.4 \text{ mm } \times 76.2 \text{ mm } \times 1 \text{ mm}$), and the bottom of the mold is also plane glass just like first type mold. The pictures are shown in figure 4.6 and figure 4.7.



Figure 4.6 the oblique drawing of second type mold



Figure 4.7 the photo of the second type mold

The third type mold was also made of glass, but the volume and thickness of mold wall are different to the second type mold. Because of the dispersion of Nafion[®] is expensive, the third type mold was designed as a small volume mold to decrease the quantity of usage of Nafion[®] dispersion. The wall of the mold is composed of cover glasses, and the bottom of the mold is composed of glass slide. The pictures are shown in figure 4.8 and figure 4.9.



Figure 4.8 the oblique drawing of third type mold



Figure 4.9 the photo of the third type mold

The next is forth type mold. The forth type mold is a variation of third type mold. So, the material used to make forth type mold is the same of third type. The main difference between this two type molds are the width of the mold. The width of the forth type mold is about 0.3 mm so the manufacturing procedure is more complicated than third type mold. The key points are how to fix the distance between the two cover glasses and how to keep the parallel arrangement of the two cover glasses during manufacturing. The main purpose of forth type mold is to make a very thick and very narrow IPMC strip by vertical casting technique. The vertical casting will also be illustrated later. Pictures of forth type mold are shown in figure 4.10 and figure 4.11.



Figure 4.10 the oblique drawing of forth type mold



Figure 4.11 the photo of the forth type mold

In fact, the forth type mold doesn't need a bottom. Because the gap between the two cover glasses are really small. So the capillary phenomenon is strong. The solution that pouring into the mold wouldn't leakage out. But the bottoms of the molds still need to avoid coming into contact with the table. So, a shelf was be designed and applied. The pictures are shown in figure 4.12, 4.13, 4.14 and 4.15.



Figure 4.12 the oblique drawing of the shelf



Figure 4.13 the oblique drawing of the assembly of forth type mold and shelf



Figure 4.14 the photo of the shelf



Figure 4.15 the photo of the assembly of forth type mold and shelf

But the forth type mold has a great problem. Due to the small distance between the two cover glasses and the flexibility of the thin cover glasses, the capillary phenomenon would be very significant. Indeed, the cover glass has obvious flexibility. And the solution that poured into the mold has cohesion force. So the distance between the cover glasses would be changed. The changing of the distance could cause the not uniform capillary force distribution, and the manufacturing would be failed because of the not uniform distribution of the dispersion in the mold. The figure of illustration is shown in figure 5.16 and 4.17.



Figure 4.16 the concept of deformation of forth type mold



Figure 4.17 the photo of the not uniform distribution of dispersion

Due to the failure of forth type mold, the fifth type mold was designed to solve the problem. The main reason of the failure of forth type mold is the flexibility of the thin cover glasses is really great in this scale (the distance between the two cover glasses is only about 0.3 mm). To avoid the problem, the glass slides were be used. Because of the glass slides are thicker than cover glasses; the deformation due to the flexibility is smaller than cover glasses. In fact, if the force applied on glass slides was big enough, the deformation would still be very obvious. Fortunately, the cohesion force of Nafion[®] dispersion is not big enough to induce the phenomenon on glass slides. The figures are

shown in figure 4.18 and 4.19.



Figure 4.18 the photo of the fifth type mold and the uniform distribution of dispersion



Figure 4.19 the illustration of the assembly of the fifth type mold

4.4 The Pouring of Dispersion

To pour Nafion[®] dispersion into a mold, a 3 mL cheap plastic dropper was be used. The photo is shown in figure 4.20.



Figure 4.20 the 3 mL plastic dropper

The pouring process of first type, second type and third type are easy. But the pouring process of forth type and fifth type has a problem. Because of the narrow gap of the mold, the injection of Nafion[®] dispersion seems to be a precise motion. And a 1 mL plastic syringe was also be used. The photo is shown in figure 4.21.



Figure 4.21 the 1 mL plastic syringe

In fact, after the test of the injection process, the 3 mL plastic dropper is precise enough.



Figure 4.22 the droplets injected in a mold

4.5 The Drying Process

After the pouring process, it needs time to let the dispersion dry. The problems that would occur in the process are listed below.

- 1. the break of membrane
- 2. the estimation of time
- 3. the control of the thickness of membrane

The main problem is the break of membrane. The internal stress occurs during the drying process of Nafion[®] dispersion due to the shrinkage of the polymer. So the fixing process of the membrane is important. The break of membrane usually occurs at the first time cast of dispersion. The following are four examples of second type mold and fifth type mold. The first two examples are the fabrication of 2 mm and 1 mm thickness chunks of Nafion[®]. And the last two examples are the fabrication of vertical casting membrane. The heights of the membranes are about 3 mm. First, two second type mold were made, and the dimensions of the two molds are about 4 cm (L) \times 2 cm (W) \times 2 cm (H) and 7 cm (L) \times 2 cm (W) \times 2 cm (H). Second, two fifth type mold were also made, and the dimensions of the two molds are both about 3 cm (L) \times 0.04 cm (W) \times 2 cm (H). But one of the fifth type molds has a glass slide bottom. Then, a quantity of Nafion[®] dispersion was poured into the four molds. After several times of pouring of Nafion® dispersion, the membrane reached the goal thickness. But, there were several fissures in the two chunks and the membrane which manufactured in the bottom-added fifth type mold, as shown in figure 4.23, 4.24, 4.25, 4.26, 4.27 and 4.28. There is a special phenomenon in the bottom-less fifth type mold. The membrane manufactured in this kind of fifth type mold almost has no fissures. It is a coincidence to design out this kind of fissure-less mold.



Figure 4.24 the side view of the fissures of the 2 mm thick chunk



Figure 4.26 the bottom view of the fissures of the 1 mm thick chunk



Figure 4.28 the side view of fissures of the vertical casting membrane in the 0.4 mm wide

bottom-added fifth type mold

Then, the bottom-added fifth type mold was abandoned. Because the bottom-less fifth type mold is obviously better than that mold.

Then, the fixing process should be applied to the chunks. To fix the fissures, pouring a little quantity of Nafion[®] dispersion in the mold, until the chunks submerged in dispersion. Then, wait for the dispersion drying. Finally, the whole chunks were finished, as shown in figure 4.29, 4.30, 4.31, 4.32 and 4.33.



Figure 4.29 the top view of the 2 mm thick whole chunk



Figure 4.30 the bottom view of the 2 mm thick whole chunk



Figure 4.32 the side view of the 1 mm thick whole chunk



Figure 4.33 the oblique view of the membrane in the bottom-less fifth type mold

After several days, the chunk would keep shrinkage, and the chunk looks like to be light 1896 yellow, as shown in figure 4.34, 4.35, 4.36 and 4.37.



Figure 4.34 the top view of the 2 mm thick light yellow chunk



Figure 4.36 the oblique view of the 1 mm thick light yellow chunk



Figure 4.37 the side view of the 1 mm thick light yellow chunk

If the requirement of precision of the product is high, the estimation of time and the control of thickness are not easy. Because the Nafion[®] will shrink during the drying process, and the residual fragment on the mold wall causes the tolerance of the estimation of quantity of Nafion[®] dispersion. The breaking of the membrane also causes problem in the estimation of time. Because re-pouring process may not need only one time. And the thickness would also be influenced.

4.6 The Heating Treatment

The actual heating process is heating the membrane up to 100 $^{\circ}$ C for 40 minutes to fully evaporate the volatile components that still remain in the membrane. Then increase the temperature up to 120 $^{\circ}$ C also for 20 minutes. After that, rises the temperature up to 160 $^{\circ}$ C for 10 minutes. Then turn off the oven to let the film decrease temperature naturally. That is an annealing process to let the molecules in the film arrange slowly to avoid the internal strain occurs. The concept of actual heating progress is shown in figure 4.38.



Figure 4.38 the concept of heating progress

The apparatus used in this heating treatment is the simple vacuum oven, composed of a rotary vane vacuum pump and a vacuum chamber, as shown in figure 4.39, 4.40.



Figure 4.39 the rotary vane vacuum pump



Figure 4.40 the vacuum chamber

The vacuum apparatus is very simple, so the heating treatment also did not be progressed precisely. Although the temperature and the vacuum circumstances did not be controlled 1896 well, the sample treated was still usable. The following are the photos of the samples, said above, after the heating treatment.



Figure 4.41 the top view of the 2 mm thick chunk after heating treatment



Figure 4.42 the side view of the 2 mm thick chunk after heating treatment



Figure 4.43 the bottom view of the 2 mm thick chunk after heating treatment



Figure 4.45 the oblique view of the 1 mm thick chunk after heating treatment


Figure 4.47 the side view of the vertical casting membrane after heating treatment

To get out the membrane from the narrow mold, a burin blade was inserted into the mold to separate the two glass slides, as shown in figure 4.48.



Figure 4.48 the side view of the vertical casting membrane after heating treatment

After the separation, DI-water was injected to let the membrane swell, so the membrane would leave the glass slide by itself, as shown in figure 4.49.

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Figure 4.49 The membrane swelled and left the glass slide.



Figure 4.50 The membrane was picked up by a stainless steel tweezers.

An obvious phenomenon was found in the vertical casting membrane. The color of the nembrane has a gradient. From the bottom to the top of the membrane, the color become more and more light, from deep brown to the very light yellow. The samples showed in this chapter would be treated with the coating process in the next chapter.

4.7 The Fabrication of the Very Narrow and Very Thick IPMC Sample by Vertical Casting Method

To realize the idea brought up in chapter 4, the vertical casting method was designed. And the sandwich structure is introduced below.



Figure 4.51 the sandwich structure of vertical casting IPMC

The bottom of the structure is a thin layer of Nafion[®], the purpose of the layer is to avoid the lower electrode break to pieces. Because the bottom of this IPMC is more dry than any other upper layers, as shown in figure 4.50. If let the electrode layer be the bottom layer, the electrode would be very dry, and would break before heating treatment, as shown in figure 4.52, 4.53.



Figure 4.52 a multi-layer IPMC under producing



Figure 4.53 The example of broken electrode

The dispersion used to make electrode layer was made by mixing Nafion[®] dispersion with silver powder. By trial and error method, the proper mixture density is about 0.060g / 1c.c. (Nafion dispersion). The improved electrode is shown in figure 4.53.



Figure 4.54 the improved electrode

And the IPMC sample is shown in figure 4.55.



Figure 4.55 a complete IPMC sample made by vertical casting method

V. COATING OF ELECTRODES ON NAFION[®] MEMBRANE SURFACE

One of the main composite layer of IPMC is the electrode on surface. There are many kinds of method to coat an electrode on Nafion[®] membrane. In this project, the electro-less coating technique was used.

5.1 Fundamental Concept

Electro-less coating is a kind of chemical method to coating electrodes on various materials. For instance, glass, PCB (printed circuit board), and, the main material in this project, ion exchange membrane. The electro-less coating in this project is according to the following chemical reaction.

$$\begin{aligned} 2AgNO_3 + 2NaOH &\rightarrow Ag_2O \downarrow + H_2O + NaNO_3 \\ \textbf{ES} \\ Ag_2O + 4NH_3 + H_2O &\rightarrow 2Ag(NH_3)_2OH \\ 2Ag(NH_3)_2OH + C_6H_{12}O_6 &\rightarrow 2Ag \downarrow + C_6H_{11}O_7NH_4 + 3NH_3 + H_2O \end{aligned}$$

First, mix the silver nitrate ($AgNO_3$) solution with sodium hydroxide (NaOH) solution. Then, the brown silver oxide (Ag_2O) precipitation would precipitate. The second step is mixing the ammonia (NH_3) with the reactant solution. The brown silver oxide precipitation will be dissolved, and the solution will be achromatic. The final step is mixing the glucose ($C_6H_{12}O_6$) solution with the reactant solution. The silver (Ag) precipitation will precipitate.

5.2 Apparatus and Chemicals

The apparatus, consumables and chemical materials used in coating process is listed below.

Apparatus :

1. Electronic balance: Precisa[®], XS 365M

- 2. Heater: Elifemall[®], Electronic warmer
- 3. Ultrasonic cleaner: DELTA[®], D80
- 4. Stainless steel precision tweezers: XYTRONIC[®], SS-sa

Chemical materials:

- 1. Silver nitrate (AgNO₃), Fisher[®] Chemical, SS73-100 (0.1 N, 100 mL)
- 2. Sodium hydroxide (NaOH), unknown, degree of purity: 99.3%, solid state granule
- 3. Ammonia solution(NH3), SHOWA® Chemical, reagent degree, 28% GR, 500 cc
- 4. Glucose ($C_6H_{12}O_6$), SHOWA[®] Chemical, reagent degree, 500 g
- 5. Ethanol (C₂H₅OH), Taiwan Sugar Corporation[®], 95%, 500 cc
- 6. DI-water (deionized water)
- 7. Nafion[®] N-117 membrane, DuPont[®], 30cm × 30cm, 1100EW, 0.7 inch thickness

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Consumables :

- 1. Syringe, TERUMO[®], 1 cc
- 2. Plastic dropper, unknown, 3 mL
- 3. Conical tube, BD Falcon[®], 15 mL
- 4. Glass slide, $FEA^{\text{(B)}}$, 1 inch × 3 inch, thickness: 1 ~ 1.2 mm

5.3 Chemical Processing

The preparation of Ag(NH₃)₂OH solution:

- Step 1. Use the electronic balance to get 0.02 g NaOH granules, and put the NaOH granules into a conical tube. Then add 8 cc DI-water into the conical tube to solve the NaOH.
- Step 2. Pour 0.5 cc silver nitrate solution into the same conical. Then the brown silver oxide precipitation would precipitate.
- Step 3. Inject about 0.2 cc ammonia into the same conical. Then put the conical into the ultrasonic cleaner to shake the solution. If the solution still not be colorless, inject more ammonia into the conical until the brown precipitation disappears.

The preparation of $Ag(NH_3)_2OH$ solution is finished.

Then the Nafion[®] N-117 membrane should be submerged into the $Ag(NH_3)_2OH$ solution for about 1 ~ 2 hours.

The steps of reduction:

- Step1. Use the electronic balance to get 0.15 g $C_6H_{12}O_6$ powder, and put the $C_6H_{12}O_6$ powder into a conical tube. Then add 6 cc DI-water into the conical tube to solve the $C_6H_{12}O_6$.
- Step2. Use the precision tweezers to get the Nafion[®] N-117 membrane, said above, from the conical.
- Step3. Mix the glucose solution and alcohol at the volume ratio about 1:1. And pour the mix solution in a petri dish. The quantity of solution should be enough to let the Nafion[®] N-117 membrane submerge in it.
- Step4. Heat the Nafion[®] N-117 membrane on the heater with a glass slide below it, until the solution on the membrane surface is dried.
- Step5. Put the dried Nafion[®] N-117 membrane into the petri dish.
- Step6. Heat the petri dish on the heater for about 30 minutes until the solution is almost dried. The electrodes would emerge at the surface of the Nafion[®] N-117 membrane.
- Step7. Heat the membrane on the heater, until the solution on the membrane surface is dried. The coating of electorde is finished.

5.4 Several IPMC Samples Made with Different Basis Materials and the Test of Electrode

Due to the different manufacturing process, the characteristics of Nafion[®] membrane would be different. So, there are three different kinds of Nafion[®] membrane, made by different methods, would be tested by electric meter. The internal resistance of the electric meter is about $0.3 \sim 0.4$ ohm.

The first type is the Nafion[®] N-117 membrane. And the electrode on the membrane has two kinds of distributions. The first kind is the most common distribution; the two surfaces of the membrane were coated with silver, as shown in figure 6.1.



Figure 5.1 the first kind electrode distribution of first type membrane



Figure 5.2 the measurement of the first kind electrode distribution of first type membrane

The second kind distribution is used to demonstrate the approximately linear actuator, as shown in figure 5.3. Electrodes were successfully coated on the narrow edge of the membranes.



Figure 5.3 the first kind electrode distribution of first type membrane



Figure 5.4 the measurement of the second kind electrode distribution of first type

membrane



Figure 5.5 the measurement of the marginal electrode resistance of the second kind electrode distribution of first type membrane



Figure 5.6 the close-up of the measurement of the marginal electrode resistance of the second kind electrode distribution of first type membrane

The second type is the self-made Nafion[®] membrane, made by casting method with second type mold. The samples are 1 mm thick and 2 mm thick. These are the same samples said in chapter 5, as shown in figure 5.7, 5.8 and 5.10.



Figure 5.7 the first kind electrode distribution of 2 mm thick self-made membrane



Figure 5.8 a drop of DI-water on the 2 mm thick membrane

The droplet on the membrane implies the hydrophobic characteristic of the electrode.



Figure 5.10 The 1 mm thick self-made membrane was coated with silver.



Figure 5.11 the measurement of surface resistance of the 1 mm thick IPMC

The third type is also a self-made Nafion[®] membrane, but it was made by vertical casting 1896 method with fifth type mold, as shown in figure 5.12.



Figure 5.12 the photo of electrode-coated vertical casting membrane



Figure 5.13 the measurement of the electrode-coated vertical casting membrane

5.5 The Adhesion Ability Test

The adhesion ability of this kind of soft basis material is very important. Because, the IPMC is a kind of soft bending actuator, if the electrodes do not tough enough, the actuator will be failed. The following are several simple tests. The samples used in this test are Nafion[®] N-117 membranes coated with first kind electrode distribution, as shown in figure 5.14.



Figure 5.14 the sample used in the test



Figure 5.16 measurement of resistance after the bending of the sample The bending test has no influence to the electrode on the surface.

The scraping test was executed by using the probe of the electric meter. After about 40 times scraping back and forth on the both side electrodes of another sample, a small, transparent gap appeared, as shown in figure 5.17.



Figure 5.18 the photo of cross section under microscope (40X) The thickness of the electrode is about 2 ~ 3 μ m.

5.7 The Conclusion of the Electro-less Coating Technique

The coating technique exhibited above has several benefits.

1. Short time:

Traditional electro-less coating needs more than 24 hours. But the technique exhibited in this texture needs only about 3 hours.

2. Low surface resistance:

Generally, to lower the surface resistance than 0.5 ohm needs three layers coating by using traditional technique. The method used in this project needs only one layer to reach the goal.

3. Low cost:

The materials used in the coating process are cheap. The total cost to coat a 10 cm² surface is about 10 NTD.

4. Good adhesion

The adhesive ability of the electrode is very well. The bending test showed above had confirmed the characteristic.

VI. EXPERIMENTS OF IONIC POLYMER METAL COMPOSITE (IPMC)

6.1 The Architecture of the Test

The architecture of displacement test is composed of an adjustable power supply, an IPMC sample, a glass sample clip and a sheet of graph paper, as shown in figure 6.1, 6.2.



Figure 6.2 the photo of the test apparatuses

The operation of IPMC can be classified into wet operation and dry operation. The wet operation means the IPMC keeps in wet condition during the actuation. The dry operation means the IPMC keeps in opposite condition.

6.2 The Operation Test

Usually, an IPMC sample is operated at a wet condition. The following will exhibit wet operation test first, and then dry operation.

The wet operation: The IPMC sample should be submerged into DI-water or an electrolyte solution, such as NaCl solution, for a few minutes before operation.

1. An IPMC made with Nafion[®] N-117 membrane, operated at 2.5 V and 20 mA.



Figure 6.3 the 4.5 cm long and 1 cm wide IPMC sample



Figure 6.4 the sample at start position



Figure 6.5 the sample performed the largest displacement After the actuation, the sample was broken due to the electrolysis of H₂O, as shown in figure 6.6. And the copper electrode on the sample clip was also electrolyzed, as shown in 1896



Figure 6.6 the sample with broken electrode



Figure 6.8 the 1 mm thick IPMC sample



Figure 6.10 the 1 mm thick IPMC performed largest deformation

The silver coated on the membrane surface would be electrolyzed. And the electrolyzed silver ions would perform the electrophoresis phenomenon on surface. The electrophoresis of silver ions would cause the short of two electrodes on the opposite surfaces. The comparison is shown in figure 6.11, 6.12.



Figure6.11 the clear edge of the IPMC before operation



Figure 6.12 the edge covered with silver after operation

In fact, the effect appears at IPMC samples with any thickness. So the edge of IPMC needs to be cleared after operation. And the surface electrode was also broken, as shown in figure 6.13.



Figure 6.13 the broken electrode 1896 3. A 2 mm thick IPMC sample, operated at 5 V and 30 mA.



Figure 6.14 the 2 mm thick IPMC sample



Figure6.16 the 2 mm thick IPMC performed the largest displacement The 2 mm thick IPMC almost did not perform any deformation. But the comparison of the two photos shows there had a slight bending at the tip of the IPMC.



Figure 6.18 the electrophoresis phenomenon on the edge



Figure 6.19 the broken electrode of 2 mm thick IPMC

The dry operation: The dry operation usually needs higher voltage than wet operation, and **1896** the displacement is also larger than wet operation. Although, in the wet operation can also apply high voltage on a sample to induce larger displacement. But, in order to reduce the electrolysis of water, a lower voltage usually be applied. The defect of dry operation is also the broken of sample, but the reason is the scorching on the electrode induced by current. So the dry operation does not a main drive method. In this text, one piece of IPMC sample made with Nafion[®] N-117 membrane was chosen to be test under dry condition. 1. An IPMC made with Nafion[®] N-117 membrane, operated at 24 V and 20 mA.



Figure6.20 the 2 cm long and 0.5 cm wide IPMC sample

Figure 6.21 the IPMC sample at start position



Figure 6.23 the electrode of the sample was broken



Figure6.24 the magnifier image of the broken electrode The syringe needle at the lower left is 0.4 mm in outer diameter. The black dots may be the position where the density of current is high.

6.3 The Test of the Very Narrow and Very Thick Samples

These kinds of samples were made by two kinds of methods. The first kind method is to coat electrodes on the edge of membrane, as shown in figure 6.3. The other method is using the vertical casting method to directly manufacture a multi-layer IPMC, as shown in figure 5.55. The architecture of the test of the samples is as the same as previous samples. And the IPMC strips were operated in wet condition. The tests are shown below.

1. IPMC made by vertical casting method, operated at 2 V and 10 mA.

The sample in the following image of the test is an IPMC with unimproved electrode. The electrode was broken, but it still could be actuated. Because of the deformation of the IPMC strip was really small, the image were captured under a 15X magnifier.



Figure 6.26 the side view of the very narrow IPMC



Figure 6.27 the test platform of the 3 cm long IPMC



Figure6.28 the IPMC before actuated



Figure 6.29 the magnifier image of the IPMC strip at start position

The syringe needle at the lower left is 0.4 mm in outer diameter.



Figure 6.30 the IPMC sample at largest deformation position

Compare the figure 6.28 and 6.29, the surface of the sample has a very obvious electrophoresis phenomenon of silver, and the nearby of the electrodes became black.

2. IPMC strip made with Nafion[®] N-117 membrane, operated at 2 V and 10 mA.

The sample did not perform any deformation, even when observed under the 15X magnifier. The following is the photo of the sample after actuated.



Figure 6.31 an IPMC with improved electrode after actuated

The sample has the same phenomenon with above sample. But the actuation of the sample was fail.

6.4 The Comparison of the Samples

The testing results are listed in the table shown below. These six samples were made by different methods, including three different kinds of membrane fabricating methods and two different electrode fabricating methods. The dendrogram is shown in figure 6.32.



The main goal in this project is to make a very thick IPMC strip by using same quantity of Nafion[®], so the very thick IPMC is also very narrow, the idea has been shown in chapter 4. The other samples made in other form were used to establish the fundamental concept of the performance of typical IPMC samples. After the fabrication and experiments of the typical IPMC sample, the very narrow and very thick IPMC strips were also made and tested.

The samples have different dimensions, and the voltage used to actuate the samples was also different. All the samples were tested under wet condition except the No. 6 sample.

The test of No. 6 sample is an additional experiment beyond the original plan. But the test result of No. 6 sample may have some value of comparison. So the test result is also listed in the table, as shown in table 6.1.
No. of sample	Dimensions (L×W×T)(mm)	Fabrication Method	Applied voltage(V)	Applied current(mA)	Max Displacement(mm)	The time of moving to the max displacement from the start position (s)
1	45x6x0.183	Nafion® N-117 membrane coated with silver electrode	2.5	20	7	4
2	32x8x1	Casting method fabricated membrane coated with silver electrode	5	20	10	40
3	20×8×2	Casting method fabricated membrane coated with silver electrode	5	30	<1	20
4	30x0.2x3	Vertical casting method fabricated IPMC	2	10	1.5	40
5	20×0.183×3	Nafion® N-117 membrane coated with silver electrode	² ES	10	Did not be observed.	The displacement did not be observed.
6 (dry operation)	20x5x0.183	Nafion® N-117 membrane coated with silver electrode	24 1896	20	20	20

Table 6.1 Experimental results of the IPMC samples

The No. 1 sample is a most common type IPMC, the test result is used to be a reference to the other test results. The No. 2 and No. 3 samples are thicker IPMC strips, and they are the same form to the No. 1 sample. The max displacement of No. 2 sample is larger than No. 3 sample. Although the displacement of No. 1 sample is smaller than No. 2 sample, but the applied voltage of No. 2 sample is larger than No. 1 sample. And the total movement time of No. 2 sample is 40 seconds, ten times of the No. 1 sample. So, a little larger displacement of No. 2 sample is reasonable. Via the above comparison, a simple and obvious trend emerges. The trend is: The thicker the IPMC strip the smaller the max displacement. And the No. 4 sample was also show the trend. Although the No. 4 sample was designed to be an approximate linear IPMC. But the test result shows the assumption in the chapter 4 is wrong. Because the small displacement means a small change in

curvature. A key point of the assumption is the change of the curvature is big for a thick IPMC. Then the approximate linear actuator would be accomplished. But the actual experiment result improve the assumption is wrong. Furthermore, compare the figure 7.26 and 7.27, the same conclusion would also be established.

The No. 5 did not be observed any displacement, and the reason is not obvious. But a probability is the electrode on the edge was too thin to control the membrane. The electrode coated by electro-less method is about $2 \sim 3 \ \mu$ m. It is really thin contrast to the vertical casting electrodes. The electrode can only control the nearby ions and water molecules. So the thin electrode can only control the nearby section. The nearby section is also very thin contrast to the whole membrane. So the membrane can not be actuated by the electrode.

The No. 6 sample performed a significant displacement under high voltage. And the electrode broke immediately; the durability of a sample under the dry operation is a problem.

VII. CONCLUSIONS

7.1 Several Defects in the Project

Although, the IPMC strips were made, the actuation ability is not good. The main reasons of the problems are listed below.

1. The heating treatment of membrane:

The membrane made by casting method needs the heating treatment. And the heating process is a very important factor to influence the characteristic of the membrane. Different heating treatment temperature and time cause the different mechanical strength, dissolution ability in water and organic solutions, color of the membrane and most of all, the absorbency of water and ionic solution. The absorbency of water and ions is very critical to the actuation ability of IPMC.

2. The coating technique

Although the coating technique has the benefits said above. And to the best of our knowledge, this coating technique is really fast, cheap, low surface resistance and good in adhesion ability. And, another important benefit is the stability of the chemical reaction. If the reaction was very fragile, the coating process of electrode would be difficult to repeat. But, the durability is not good; the electrodes on the membrane are easy to be broken. No matter the electrolysis of water or the high voltage are easy to break the electrodes.

7.2 Future works

1. To the heating treatment:

The apparatus used in the heating treatment is the simple vacuum oven system as shown in figure 5.39, 5.40. The temperature control of the oven is not precise. The tolerance of the temperature is usually about 10 centigrade. But, most of all, the temperature and time of the heating process should be lower and shorter. The membrane should be more flexible and the absorbency of water should be better.

2. To the coating technique:

To improve the coating technique, a better heater should be used. The temperature distribution of the heater used in the experiment is not uniform. The temperature of the heater in the center is about 85 centigrade, and the temperature at the edge is about 50 centigrade as shown in figure 7.1, 7.2.



Figure 7.1 the central temperature of the heating plate



Figure 7.2 the side temperature of the heating plate

So the difference in temperature is big. Another important caution is the concentration of the $Ag(NH_3)_2OH$ solution, if the concentration of the $Ag(NH_3)_2OH$ solution is very high (about 10 times to the concentration listed in the chapter 6). The solution may explode when the solution is almost dried.

3. To the very thick and very narrow IPMC strip

Although the idea of approximate linear actuator failed, but the idea of the very thick and very narrow IPMC strip was accomplished. Use the vertical casting method can really make a thick IPMC with a small quantity of material.



REFERENCES

- [1]. Y. Bar-Cohen, "Electroactive polymers as artificial muscles capabilities, potentials and challenges," Section 10 in Chapter 8, "Motion" paper #134, <u>Handbook on Biomimetics</u>, Yoshihito Osada (Chief Ed.), publisher: NTS Inc., Sept. 2000, pp. 936-950 (in Japanese).
- [2]. Jet Propulsion Laboratory, Pasadena, Calif. (2005,July 10). Artificial Muscles Get a Grip on Human Hand [Online]. Available: <u>http://www.nasa.gov/vision/earth/technologies/arm-022805.html</u>
- [3]. 方柏凱, "應用 IPMC 致動器於變曲率主動式心導管發展", 第八屆奈米工程暨微系統技術研討會, 2004.
- [4]. Kim, B., Lee, S., Park, J.H., Park, J.O. (2005a), "Design and fabrication of a locomotive mechanism for capsule-type endoscopes using shape memory alloys (SMAs)", IEEE/ASME <u>Transactions on</u> <u>Mechatronics</u>, Vol. 10 No.1, pp.77-86.
- [5]. Shahinpoor; Mohsen (Albuquerque, NM), Shahinpoor; Parsa (Albuquerque, NM), Soltanpour; David (Larchmont, NY). (2003,January 16). Surgical correction of human eye refractive errors by active composite artificial muscle implants. [Online]. Available: http://patft.uspto.gov/netacgi/nph-Parser?Sect1=PTO2&Sect2=HITOFF&p=1&u=%2Fnetahtml%2FPT O%2Fsearch-bool.html&r=1&f=G&l=50&co1=AND&d=PTXT&s1=7090696&OS=7090696&RS=70 90696
- [6]. Nguyen T., Goo N., Nguyen V., Yoo Y. and Park S. 2008 "Design, fabrication, and experimental characterization of a flap valve IPMC micropump with a flexibly supported diaphragm", <u>Sensors Actuators</u>, A 141 640–8
- [7]. Deole, U., Lumia, R., Shahinpoor, M., "Design and Test of IPMC Artificial Muscle Microgrippers," Proceedings of 3rd World Congress: Biomimetics, Artificial Muscles and Nano-Bio (http://www.world-congress.net/), Lausanne, Switzerland, May 25-27, 2006
- [8]. K. J. Kim and S. Tadokoro (eds.), *Electroactive Polymers for Robotic Applications: Artificial Muscles and Sensors*, Springer-Verlag, 2007.
- [9]. Ronald Pelrine, Roy Konrbluh, Qibing Pei, Jose Joseph, "High –Speed Electrically Actuated Elastomer with Strain Greater than 100%," <u>Science</u>, 287, 836-839 (2000).
- [10].P. Dubois, S. Rosset, S. Koster, J. Stauffer, S. Mikhaïlov, M. Dadras, N.-F. de Rooij, and H. Shea. Microactuators based on ion implanted dielectric electroactive polymer (EAP) membranes. <u>Sensors and Actuators A: Physical</u>, 130-131:147-154, 2006.
- [11].Dr. G. Kovacs, S. Michel. *EAP Technology* @ *Empa* [Online] Available: http://www.empa.ch/plugin/template/empa/*/72289/---/l=1
- [12].Cai, L. et al. "Surface structure of ultrathin copolymer films of ferroelectric vinylidene fluoride (70%) with trifluoroethylene (30%) on graphite", <u>Phys. Rev.</u> B 70, 155411 (2004).
- [13]. Haisheng Xu, Dong Shen, Qiming Zhang, "Structural and ferroelectric response in vinylidene fluoride/ trigluoroethylene/ hexafluoropropylene terpolymers", <u>Polymer</u>, Volume 48, Issue 7, 23 March 2007, Pages 2124-2129.
- [14].M. Shahinpoor, "Electrically-activated artificial muscles made with liquid crystal elastomers", Proc.

SPIE Vol. 3987, p. 187-192, <u>Smart Structures and Materials 2000</u>: Electroactive Polymer Actuators and Devices (EAPAD).

- [15].Min-Hui Li and Patrick Keller, "Aritficial muscles based on liquid crystal elastomers", Phil Trans R Soc A 2006 364: 2763-2777.
- [16]. Ray H. Baughman, et al. "Carbon nanotube actuators", <u>Science</u> 284, p.1340 (1999).
- [17]. Shahinpoor M, Bar-Cohen Y, Simpson J O and Smith J, "Ionic polymer-metal composites (IPMCs) as biomimetic sensors, actuators and artificial muscles-a review", <u>Smart Mater</u>. Struct. 7 R15-30, 1998.
- [18].Mohsen Shahinpoor and Kwang J Kim, "Ionic polymer-metal composites: I. Fundamentals", <u>Smart</u> <u>Mater. Struct.</u> 10 819, 2001
- [19]. DuPont[™]. DuPont Fuel Cells DuPont[™] Nafion[®] PFSA Membranes NE-1135, N-115, N-117, NE-1110. [Online]. Available: <u>http://www.fuelcell.com/techsheets/Nafion%201135%20115%20117.pdf</u>
- [20].黃如慧 嚴詠聖 鄭敬熹 紀喨勝, 高分子電解質燃料電池 [Online]. Available: http://www.ch.ntu.edu.tw/~rsliu/molpdf-liu/Group05_Report.pdf
- [21].KJ Kim and M Shahinpoor, "Ionic polymer-metal composites: II. Manufacturing techniques", <u>Smart</u> <u>Material and Structures</u> 12 (2003), pp. 65–79, 2003.
- [22].Perma Pure LLC. Nafion: Physical and Chemical Properties. [Online]. Available: http://www.permapure.com/TechNotes/Nafion%20physical%20&%20chemical.htm
- [23].Mauritz KA, Moore RB., "State of understanding of nafion", Chem. Rev., 2004, 104 (10), pp 4535–4586.
- [24].H.G. Haubold, T. Vad, H. Jungbluth and P. Hiller, "Nano structure of NAFION: a SAXS study", <u>Electrochim Acta</u> 46 (2001), pp. 1559–1563.
- [25].Klaus Schmidt-Rohr & Qiang Chen, "Parallel cylindrical water nanochannels in Nafion fuel-cell membranes", <u>Nature Materials</u> 7, 75 - 83 (2008).
- [26]. DuPont[™]. DuPont Fuel Cells DuPont[™] Nafion[®] PFSA Polymer Dispersions . [Online]. Available: http://www2.dupont.com/FuelCells/en_US/assets/downloads/dfc103.pdf
- [27].Kwang J. Kim and Mohsen Shahinpoor, "A novel method of manufacturing three-dimensional ionic polymer-metal composites (IPMCs) biomimetic sensors, actuators and artificial muscles", <u>Polymer</u>, Volume 43, Issue 3, February 2002, Pages 797-802.
- [28].Sung-Weon Yeom and Il-Kwon Oh, "A biomimetic jellyfish robot based on ionic polymer metal composite actuators", <u>Smart Materials and Structures</u>, Volume 18, Number 8, 2009.
- [29].J. Rossiter, B. Stoimenov, T. Mukai, "A bistable artificial muscle actuator", Proc. 17th IEEE Int. Symp. Micro-Nanomechatron. Human Sci., pp. 35-40, 2006. Conference held in Nagoya, Japan.
- [30].M Shahinpoor and KJ Kim, "Ionic polymer-metal composites: III. Modeling and simulation as biomimetic sensors, actuators, transducers, an artificial muscles", <u>Smart Materials and Structures</u> 13 (2004), pp. 1362–1388.
- [31].Z. Siroma, N. Fujiwara, T. Ioroi, S. Yamazaki, K. Yasuda and Y. Miyazaki, "Dissolution of Nafion[®] membrane and recast Nafion[®] film in mixtures of methanol and water", <u>Journal of Power Sources</u> Volume 126, Issues 1-2, 16 February 2004, Pages 41-45.