Nafion Simultaneous Humidification and Actuation Feasibility

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ABSTRACT

The Ionic Polymer Nafion has existed since the 1960's when DuPont developed it and found that it worked for the fuel cell industry. Ionic Polymer Metal Composites (IPMC's), such as platinum coated Nafion, have been known to actuate when electrically stimulated since the 1990's.

The IPMC investigated needed to be hydrated to actuate and was reported to transmit moisture or humidity across the coated surfaces. The purpose of this research was to investigate the feasibility of a single IPMC material producing the forces needed to pump air by actuation and humidify the air being pumped as one material at the same time. The experiments simulated all the different aspects of a likely future device design where each item was isolated and investigated. Hydration was investigated without considering the effect on humidification as well as the opposite consideration. Simulation of air flow was undertaken with computer modeling to determine shapes that might allow real transmission if a pumping device were to be produced.

Determining if combining both functions was possible and, if possible, if it would be beneficial for human air respiration was the final goal of this research. Quantifying the achievable values for each task and then making comparisons of cost, efficiency and design utility against existing technology were the final metrics to draw the conclusions of this work. The study indicated that it might be possible to produce a combined effects device, but current technology would render the device expensive and inefficient compared to current solutions.

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Flow Rate of the Gas (air).. $\dot{Q}$

Temperature of the gas at interface... **T**

Pressure of the gas at interface.. **P**

Relative Humidity of gas before entering apparatus..................................... **RH in**

Relative Humidity of the gas after exiting apparatus..................................... **RH out**
Nafion film wet thickness.. **tTLw**

Nafion film dry thickness... **tTLd**

Thickness of Platinum Coating on 1^{st} side... **tPT1**

Thickness of Platinum Coating on 2^{nd} side.. **tPT2**

Area of sheet.. **A**

RHO Density (subscript for specific material e.g. water) .... ρ

,

,

Attestation of Authorship

"I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person (except where explicitly defined in the acknowledgements), nor material which to a substantial extent has been submitted for the award of any other degree or diploma of a university or other institution of higher learning."

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Signature

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10/7/2013

Date

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

The central question that this study seeks to address is this: is it possible to produce a single material that could both pump a gas, such as air, and condition the gas by humidifying it with water, using materials that could be applied in a human health setting? That is to say, combine actuation for pumping with the same material providing the humidification function? The motivation for this combination ultimately would be an air carrying pump that could deliver air at a desired flow rate and given level of desired moisture content in a medical setting. In order to be an improvement on existing technology, the material and the pump would have to offer some greater benefit than the current two step processes being used. Such improvements might include greater accuracy of delivery, reduced energy use, smaller overall device size or reduced cost; however, the purpose of this study was to determine if there is a material that could possibly produce such a combination of features in a single material, in the range of functionality required outputs for adult human use where the breathing rate is typically 12 to 20 breaths per minute or 6 to 10 litres per minute of volume [1].

An adult human needs to be able to breathe up to 10 litres per minute (or 600litres per hour) and the humidity range would typically be between 50% and 100% . An ideal candidate for building a pump that can move and simultaneously humidify the air would be one that is flexible, hydrophilic and capable of self-actuating or being able to be made to be self-actuating [2].

Given the state of material knowledge available today, through university study, global data bases and internet connectivity, and the fact that the methods to modify existing materials are growing in number and sophistication continuously, the present day was a reasonable time to pose this question because the idea of combining the two desired functions is not unthinkable. It was possible to suggest the concept of two functions in one material and there was historical precedence for this type of development in many parallel industries, such as conducting polymers in the electronics industry or selectively permeable fabrics in the sporting industry.

In order to fulfill the dual role requirement of two functions in one material, the candidate materials would need to have physical structure that can transport water and be able to demonstrate some mechanism that generates physical motion. Since the desired end uses could be electrical devices, using electricity as the motion stimulation was the chosen stimulus for the motion energy source, to provide the cause of motion of the gas. The requirements of the problem are that there is some viable moisture transport mechanism and some viable motion mechanism that could be exploited to energise the gas to move and control humidification at the same time. In considering materials, it became clear that the variety of behaviours suggested a hybrid material, so that the two aspects of the requirements could exploit the more complex performance nature of a hybrid or composite material.

1.1.1 ORGANISATION OF THIS THESIS

This Chapter will discuss a general overview of the project and what specific needs were addressed by the research. A detailed Literature Review was carried out in Chapter 2. Chapter 3 contains the research specific methodology that outlines and explains all the experimental set-ups and reasoning behind the selections and experimental designs. Chapter 4 reports the results and comments on the data and experimental collection issues. Finally in Chapter 5, conclusions and suggestions for further work are forwarded for consideration and summarization of the information reported in the first chapters of the study.

The materials that offered the unexpected benefit of significant previous development, as a starting place for this work, were established for the fuel cell industry: ionic polymers. The transport characteristics were optimised to allow ionic control and motion of liquids for the fuel cell reactions. As a group of materials, they were tough, flexible, and durable at relatively high temperatures, easily available commercially and their chemistry was well understood.

Ionic Polymers might be able to perform the water transport function of hydration, as they exist now, but that would not accomplish the motion needed for actuation of the pumping mechanism. Fortunately ionic polymers can also be coated with other materials, specifically metals, so there was significant potential to produce composite hybrids with unknown characteristics. Previous work in this area has also been undertaken and a class of materials has emerged called Ionic Polymer Metal Composites (IPMC).

Nafion with Platinum were selected for this study because the materials were well represented in the literature for physical properties that are relevant, they were commercially available and the methods to process them into a useable condition were reported in the literature and reproducible in the laboratories available for this study. Nafion shows promise as an actuator when coated with metals and Nafion shows the ability to humidify air as it comes into contact with moisture.

1.1.2 SIMULTANEOUS ACTUATION & HUMIDIFICATION

Could Nafion, a typical ionic polymer, be prepared with a metal coating in conditions to continuously humidify and actuate? If all the feasibility considerations were proven, would it be possible to build a pump that could move air and add or remove humidity from that air using a single material? Since the two functions that are of primary interest, for this study, are moving air from one point to another and humidifying the air, then the aspects to qualify immediately were: how can the material be made to move and does that process it allow humidification? Only If these two "early checks" showed promise would it have been worth pursuing all the other questions that broaden the case for true feasibility. If a negative result was obtained for either central issue, then the study would have had to consider at least one alternate material or a change in objective .

There were several ways to energize the material. Thermal energy, electrical energy or a chemical reaction all could cause movement. In a contemporary device, electrical stimulation is the most accurate, repeatable and convenient way to cause motion. Thermal input would likely be created by an electrical source. Any chemical reaction would require replenishing reagents. Electricity was the most practical solution. The literature supports electrical stimulation as a stimulation source and this method was used. Ionic swelling was investigated based on electrical stimulation.

The amount of force that the IPMC could generate was investigated with different geometric layouts. The experimental design investigated different methods of using the materials to try and determine a range of values and further determine which mode or modes of force generation were most suitable for pumping and conditioning the air.

The literature discusses a broad range of surrounding environmental boundary conditions, interactions and border conditions in the fuel cell and other applications areas for similar materials. Since the ultimate intended use for this study was human breathing applications, many of the known chemical, temperature and operating conditions of the literature were illustrative of a method but were not suitable for this work.

The human suitability needs severely reduced the utility of the literature applicability. Many of the most exciting demonstrations in the literature [3], had a significant difference of one detail or another where the changing of a single fact rendered the existence of a study irrelevant to a human use application. (e.g. micro motion moves a liquid more effectively than the same motion could move a gas due to the difference in compressibility and surface effects of the two materials). A liquid pump can exploit existing effects of the materials that an air pump cannot, due to flow continuity differences between liquids and gasses (e.g. the simple oscillating motion touching the sides of pump chamber, in a liquid pump, is a benefit and helps drive the flow by sealing the chamber on each stroke). This effect, beneficial in a liquid pump, was not a benefit for the air flow pumping application where side touches interrupted the flow. The motion is simple oscillation in both cases, but the characteristics of the surrounding fluids are better suited to the liquids. Sustainability of conditions was the next question. Could the mechanisms be sustained for a useful period of time? Once the experimental mechanisms had been quantified, durability of materials and sustainability of performance were also considered.

The specific force issue was to understand how much force could be generated by the materials and what options best convert the force into gas transporting mechanisms. The specific geometric constructions of the materials affected the answer to this experimental question. The design of the experiments was framed in a way to address what the likely use mechanisms would be and the forces that were measured were designed to compare likely values of relevance to the reported values in the literature. Producing a range of force values that could be considered representative allowed the feasibility issue to be addressed.

The material speed was related to the speed and volume of gas that would need to be transported. The flow potential relating to material motion needed to be understood while an optimised pump for air flow was beyond the study scope. The material motion was investigated in several simple flow inducing channels to gather indicative flow data. Scalability of the flow mechanisms was considered.

Water transport was investigated. Quantification of possible lab humidification under laboratory conditions where the surface area, pressure, flow rate of air and temperature were all controlled was investigated to determine realistic design and feasibility information for intended uses of interest.

In summary, the experimental questions would determine if the shape memory polymer identified could move and generate enough force to move air at a flow rate high enough for an adult human to breathe and, at the same time, add enough moisture in that volume of air for breathing. All of these issues combined to determine feasibility in this case.

1.1.3 PROCESSES TO BUILD MATERIALS

It will be very important to confirm that there is at least one process or series of processes that can be used to make a material that can be investigated systematically and repeatably. If the conditions achievable for the investigation are not repeatable or do not show the potential to be scaled up, then the phenomena being investigated are not suitable for inclusion in this study. Early experimental investigations will involve proving that a reliable and consistent method of production can be identified.

1.2 OBJECTIVES OF THIS WORK

The goals of this research were to:

- Determine if IPMC could achieve simultaneous actuation and humidification
- Confirm simultaneous mechanisms: hydration, actuation and humidification
- Investigate as coupled pairs co-existing functions
- Show hydration was possible to support actuation
- Prove that humidification was possible while actuation occurred
- Demonstrate continuous actuation during both hydration and humidification
- Confirm that no two item combination prevented the third mechanism and
- Prove evidence showed that co-existence of all three items was possible.

1.2.1 HYDRATION

Nafion hydrates easily when placed in direct contact with water (see Table 4.1). The extent to which water will be absorbed by the polymer and confirmation of any coating effects on that hydration were the two main issues to investigate. All experiments (see Methodology in Chapter 3) were designed to investigate the ability of Nafion to take water from the liquid source side and transf er it to the air side and change the Relative Humidity of the air.

1.2.2 ACTUATION

Actuation can take many forms, however for this study actuation was defined as some form of deflection or periodic oscillating from excitation. The ability for Nafion to actuate when coated with metals is well documented [4]. The speed and strength of the motion has to be investigated to quantify what the values are for purposes of design [5, 6] and verification of utility [7]. The results produced in lab conditions would need to be converted into usable mechanisms to suit the conditions needed for the intended device(s).

1.2.3 HUMIDIFICATION

Humidification by an IPMC material was defined as the ability to put moisture into a surrounding air as positive humidification. (If the material was removing moisture from the surrounding air, then that would be considered negative humidification). Humidification, like actuation, depended on sufficient hydration.

A minimum hydrated state was essential to both actuation and humidification. If the degree of hydration is close to a minimum level, then hydration becomes the critical factor in the coupled mechanisms of hydration-actuation and hydration-humidification.

1.3 MATERIAL SELECTION

Ionic Polymer Metal Composites were produced to address transport selection needs for ionic species in the fuel cell industry [8]. In fact the Ionic Polymers were invented first and then subsequent research showed that the chemical reactions of the fuel cells could be controlled and maintained by the properties of the new membranes. The polymer made the function of the application possible and then the optimization and fine tuning of the membrane created the fuel cell industry.

In the subsequent refining and investigation of the membranes, the techniques that were investigated included attempts to coat and alloy the polymer structure with outer surfaces of many materials including metals, clays, and other surface materials. Most of these techniques were developed for fuel cell applications. The enormous range of properties, modifications to these properties and enhancements of features and behaviour meant that this broad range of modifications and materials has given rise to the new class of IPMC materials which is now an area of study itself. This proliferation of study has meant that there is good literature evidence that can be used to consider the different types of Ionic Polymer and the different type of blending agents to form composites (e.g. IPMC's) or electrodes. In the 1960's there were limited composite base materials available originally from one manufacturer (DuPont). Now there are many manufacturers of the ionic polymer materials [9] and good experimental evidence for many composite constituent materials as well [10-12].

The literature shows that bimetallic style construction allows motion to be achieved when voltage is applied to the conducting surfaces of the metal coatings on a Nafion strip. Nafion shows promise as an actuator when coated with metals [13, 14] and many metals have been demonstrated to produce this effect [11]. Copper, Nickel, Silver, Gold and Platinum have all been used as metals on Nafion to produce the electrode effect desired for actuation [11, 12].

Platinum was chosen for the work due to its chemical inertness (since it is a Noble transition metal it resists oxidation or reaction to biological contaminants).

In summary, the mechanisms, processes and material are all available to test the hypothesis of this study.

CHAPTER 2: LITERATURE REVIEW

2.1 INTRODUCTION

This research came about from the respiration and ventilation work that has already been undertaken by the Institute of Biomedical Technology (IBTec) at A.U.T. [15] Certain challenges have persisted since the initial discoveries of the materials took place, suggesting the area of study or endeavour. Through the previous work it was conceived that it might be possible to humidify and pump respired air to needed patient levels of air and moisture using the same material that performed the pumping function that circulates the air [16, 17]. Current designs separate these two functions into separate systems as Chalon shows the need [18] and others investigate methods for humidification in anesthetic gases [19, 20]. In order for this concept to be successfully developed there would need to be a performance or commercial advantage (ideally both) to the new solution. If such a material and its associated mechanisms (simultaneous actuation and humidification) does exist, or could be developed, it is conceivable that it could offer size or cost benefits.

Researchers are familiar with actuation of polymers through the fabrication of IPMC actuators for artificial muscle work and other IPMC actuation applications. Whilst there are examples of IPMC actuation [21-23] and humidification [24] performed separately , specific cases of these two features being combined in the right conditions for human use were not available in the open literature. The most important purposes of the literature review, in this case, were to understand if any IPMC devices were already pumping air and humidifying it simultaneously and if this use was being made in human use devices. [22, 24-28]. Since the review did not find simultaneous actuation and humidification, the purpose of the literature review then became to understand what characteristics were in place and what had not been accomplished to try and achieve such an application [7, 29, 30].

The human body needs humidification when surgery is taking place and when recovering from surgery to support tissue health that dehydration threatens [19]. This need can extend past the hospital experience to home use [31] as well in such conditions as sleep apnea [32, 33]. Humidification of inspired gasses reduces the occurrence and severity of breathing related diseases and other problems [34]. Conditioned air reduces the risk and side effects on the patient during and after surgery to improve recovery. With an estimated 234 million surgeries performed globally in 2008-2009 [35] there is very clearly a need for humidification solutions. If the accuracy of delivery or control can be improved or the energy or cost to achieve the needed effects can be decreased, then there is a commercial benefit in combining or simplifying current designs.

In a medical application where the intention is to apply humidity in a controlled manner to air as it is being transported for to a patient's mouth, or throat, the selection of ions available is not chosen by a design performance requirement only, but can only be selected from what materials are allowed to be used with patients in devices. This safety requirement significantly limits the chemical and material choices that can be made for consideration for this specific application.

2.1.2 ACTUATION: PREVIOUS INVESTIGATIONS

Actuation was framed to suit the purpose of the motion. In the artificial muscle challenges, the amount of power generated and the time in which it can be generated have very specific constraints.

Micropump devices are currently being pursued by many groups such as Pak [36], Nguyen [37], Ramirez-Garcia [38], and Santos [29] . One that has had experiment-al success with multiple part electrode production is Santos et al [29]. Producing motion and flow have both been achieved with many novel structures and designs.

The flow rates are typically small, in the range of micro litres per second [38], but for their size, the micropumps are achieving significant flow rates for the amount of energy used and the size of their mechanisms. In fact, with the frequencies and geometries typically employed, the pumps are making use of effects that do not “scale up” to larger volume devices. The units are relying on strength-to-weight ratios where the thin film movement and control produces small amounts of force in the range of milli-Newtons and these effects are sufficient for the application. Santos et al used IPMC actuation to produce a liquid micro-pump where the rate of pumping and mechanisms deployed suited the scale of the IPMC material’s capability [29] and others such as Jeon [34], Ramirez Garcia [38] and Nguyen [37] all used actuation of IPMC material to investigate pumping. Artificial muscle was initiated by Bar Cohen [23]. In all the examples found in the literature, the current uses involve finding applications where the exiting scale of force suits the application.

2.1.3 HUMIDIFICATION

The first commercial use of humidification of air in medical processes was a critical component of patient care and an essential part of monitoring the quality of the air that a patient needs. Both the rate of change of humidity and the overall moisture content need to be monitored and controlled in order for a patient, with a given condition, to be kept in a stable condition to allow healing to take place [17, 20].

There are many current designs in use in hospitals: hygroscopic heat-and-moisture exchanger (HME) with a bacterial viral filter or hot-water humidification with a heater wire in both inspiratory and expiratory circuit limbs either Double Hot Wire (DHW) or the inspiratory limb only Single Hot Wire (SHW). Patients with asthma, airway hemorrhage, or airway burns are all candidates for humidified air supply device needs.

The humidification aspect of the design task that needs to be supported involves understanding what rate water can be transported by the composite IPMC material selected. In the Nafion Pt material selected for this study, many of the operating parameters such as chemical exposure permissible, temperature and range of electrical stimulation were relatively fixed. This being the case, understanding the effects of the characteristics (both fixed and less constricted) was an important area of consideration for humidification by the IPMC [39-41].

Again, the fuel cell studies are important as indicators of capacity and potential [24, 42, 43], but since the operating conditions of fuel cells are significantly different than the application that this study would be concerned with, it was important to consider how these differences would impact performance and how the techniques of study and imaging would need adapting or discarding if the differences were insurmountable [44, 45].

Similar to hydration, the interface scale [46] understanding of the water transport characteristics [40] would affect the ways in which the membrane was capable of carrying out humidification [47]. Novel self-supported natural and synthetic polymer membranes could be used for air humidification. The proton exchange behavior of Nafion would determine some of the characteristics of the humidification performance [48, 49].

The effect of the electric charge required for actuation was also considered in relation to the internal gel behavior and properties of the polymer as it could affect rates of humidification [13] by changing the charge relationship or the geometry of the material relative to the humidification pathway for the liquid water.

2.2 IONIC POLYMER METAL COMPOSITES

2.2.1 BACKGROUND

The class of composites that were identified in the literature and science community and for an actuator that could also humidify will need to have clear fabrication, control and consistency properties. Ionic Polymer Metal Composites were the class that could combine all the required properties in one type of material [17, 50]. The need to modify the properties of existing materials in order to combine the reported applications of pumping and humidification in one material may be a compromise of properties from existing applications, or some unreported design changes may be needed to overcome a performance or property performance issue, however, a feasibility determination will be based on the ability to demonstrate that a process is possible, rather than efficient, at the point where it is discovered. In the next sections, evidence of the types of activity that were achieved with this class of materials showed that there was obvious potential demonstrated to indicate consideration for this study.

Nafion was the original commercial perfluorinated polymer that was developed and branded by DuPont in the 1960's [8, 51]. The structure of the membrane of Nafion was suitable for fuel cells because of its select permeability and directionality of control [24]. The development of the material was achieved by continuing work on the chemistry of fluorine, however the difference with the sulphonated molecules of the Nafion polymer was that it does react with water and protons in the way that fluorine in Teflon does not [48, 52-55].

Because of all the development work on fuel cells, there was extensive and long standing literature available on the hydration characteristics of the Nafion and indeed there are also other manufacturers, now, that produce similar materials. The literature and development of fuel cell membranes goes back to the mid

1960's with the name "Nafion" appearing in over 7900 papers since 1973 to the present on one peer reviewed search engine. Flemion, Aciplex and Hyflon are all similar perfluorinated membranes that use the same mechanisms for proton transport and are very similar structurally [56]. A search in the same database for the other materials produced 79 papers for Flemion, 32 for Aciplex and 49 citations for Hyflon. Due to the overwhelming historical presence of Nafion in the research literature and the commercial market place, it was decided that this material would be used as the basis for the IPMC research for this project. If the outcome were to be that the research showed promise as a product, then reviewing the performance of any discovered mechanisms could be made as a comparison study between Nafion and other ionic polymer materials [9].

These materials were made because the direction of the chemistry that the chemists were working on suggested that this was the direction they should go to learn more. The transport properties of the membranes meant that they could improve fuel cell reactions, so there was and is a very strong motivation to work on the mechanical, proton transport and chemical properties of the membranes as well as the best morphology understanding possible for the materials. The existence of the membranes gave researchers new opportunities to try to modify the properties of the membranes, to come up with alternative uses to the membranes from that of fuel cells. Any fuel cell related discovery will be absorbed into all the other areas where applications are also being based on Perflourinated

Membranes.

In 1992 it was realised by Bar-Cohen that the reverse process of a fuel cell could be employed as an actuator. That is, electrical activity could cause motion in a membrane that had surface electrodes attached to it. Asaka et al [57], Shahinpoor [27] and Sadeghipour et al [58] all were working on research that was based on these phenomena in the same year [17] . Once the observation was made that the reverse pathway of the fuel cell mechanism could be turned into motion, the opportunities to work on variation of extent and purpose were as broad as the needs for motion itself.

The basic properties needed for actuation and humidification are conflicting in many respects: flexible and metallic, water transporting and metallic, electrically conducting and polymer all could be incompatible property and material behavior matches if it were not for the blending behavior of composites. Ionic Polymer Metal Composites are made by coating Ionic Polymers, such as Nafion, with thin layers of metal on one or both sides of the polymer base. The individual characteristics of each material and the proportions of their combination, as well as the way that they are combined, produced a true composite material where the properties are a blend of each of the properties of the constituent materials. In some cases such as water transmission, the combined effect of the two materials produces an effect that is better than either material on its own.

The solution set of what materials could exist which are capable of embodying the correct properties is not a large number of materials. In order for a material to work it would need to be flexible, capable of moving with enough force [27] and speed to pump air down a tube [25, 26] and delivering humidification to the air, while being chemically inert and non-toxic to all human biology. It is unlikely that such a material would exist in nature and not have been identified and reported already. This being the case, it is likely that the requirements are too distinct for a single constituent material to fulfill all the design needs. It is for this reason that hybrid composite materials became the centre of focus for the literature search and the study [22, 23]. Composites are purposefully fabricated with a view to combining as many desired characteristics as possible and also at the same time overcoming any of the undesired side effects of the fabrication and utilization methods. One of the important aspects of composites is that there are often controls available to refine and fine tune a variable or set of variables such as the quantity or degree of components and most aspects such as thickness and chemical composition, as well as physical properties [21, 22]. If the basic concept can be established, composites offer enormous latitude to produce an optimised solution [17, 39, 59].

2.2.2 APPLICATIONS UTILISING IPMC

Based on the many properties revealed through the research undertaken, devices were produced. These devices exploited the various benefits and could yield insight for our device development. A “Swimming Fish” toy [50] was one of the earliest commercially available uses of IPMC that performed actuation to facilitate movement. The need for the material to remain consistently hydrated was cleverly solved by the toy remaining in water all the time. This type of matching the limitations to the output is easily achieved when the builder of the toy defines all the output entirely. If the power available from the power source is a certain size, then the fish and parts can be made to suit that size. This same thinking was applied to the humidification and pumping tasks. For example if the actuator strip is only 1/4000th of the needed force, it was clear that the solution could employ 5000 actuator beams to solve this issue. The solution may not have been cost-effective, but it may indicate that the method is possible and further refinements could produce a result with 2000 beam filaments and later only 1200 and so on.

As is the case with most historical materials development, a new material or method of processing is developed that finds a specific use and then as the modification to that material and technology take place, more and more uses are found for the materials. The actuation motion was used for novelty when the control and strength issues were not well understood. It has been the case repeatedly in the history of science that an observed phenomena is utilised before it is fully understood such as gravity [60]; feasibility is often established in this middle ground of knowledge. The same approach was taken with this research. The intention is understood, but because the mechanisms needed for the application are not expected, the literature to support the application was not in place directly. There was a paradigm shift to run the sequence backwards to arrive at actuation from fuel cell membranes. Similarly, there are obstacles to overcome to use the membrane as a humidification surface for air and an actuator at the same time.

Reviewing the literature, it was clear from the early IPMC papers that the polymer membrane material of the electrolyte being hydrated is essential for motion [4, 5, 57]. As the degree of hydration decreases, so does the activity of deflection [61] . This relationship between hydration and actuation has been understood since the 1999 Smart Structures and Materials - Electroactive Polymer Actuators and Devices Conference in Newport Beach, CA, USA [61]. Ultimately, if the degree of hydration falls low enough, all movement ceases. The specific percentage of hydration needed will depend on all the variables of the system. Major factors contributing to this actuation behaviour are membrane thickness, nature of electrical stimulation applied with all the frequency, potential difference, amplitude and phase variations producing different results; thickness, shape, preparation and materials of electrode construction, ionic species of the end chain on the electrolyte membrane and the solutions that it is interacting with, age of the material, size of the electrode and the proportions of the size relative to the shape. With all these variables contributing to the degree of actuation possible under ideal conditions, it becomes clear that there is not one single ideal value for hydration to make the process of actuation work. What is easy to see is when there is not enough hydration, since the electrode moves less and less and then just stops.

The transport of water in the membrane from the surface takes place in two principal ways: electrostatic transport between ion and water dipoles and the effect of the size of the cation and its hydrophilic effect on the membrane [40, 62]. This suggests that if you have control over your surroundings for design of the environment, you would choose optimised ionic constituents to improve the water retention and energy transfer characteristics of the membrane when being actuated. Any ion species that increased water uptake and retention to allow persistent membrane actuation would be “selected in favour” over ions that prevented or diminished water uptake in the membrane.

Nafion, itself, was not the only Ionic Polymer that could have been selected for this study. Nafion was selected for this work for two principal reasons. Nafion had the most history and related literature. This could help support thinking around new outcomes if results needed interpretation. Convenience was the other factor since sourcing commercially available Nafion was more accessible than any other Ionic Polymer in Australasia.

Motion and the use of polymers as actuators have been the focus of many researchers for the purpose of simulating muscle to produce “robot like devices”. Artificial muscle [63] is certainly one such area of activity and must be considered an “holy grail” of actuation accomplishment. In addition to artificial muscle applications, being able to build reliable cost-effective micro-pumps is an area where devices and properties are being exploited when the scale is suitable. Given the frequency of movement, and the amount of force that can be generated, the pumps are really only suitable for small volume, small force applications where a source of continued hydration is available to keep the Ionic Polymer material hydrated and in a suitable condition to actuate. This point was particularly relevant to this study since there were pump examples that were able to generate the force to pump liquids through clever and ingenious valve design, but the flow issues that surrounded air pumps were not as suitable to the force generation or scale available for IPMC’s as those surrounding liquid pumps [38]. The pump device examples are often intended for liquids and the feature that distinguishes their frequent success is the existence of some form of flap valve in the design [3, 29] or utilization of multi-layered IPMC construction of the pumping portion of the application [37]. One of the areas where many devices benefit from significant recent advancements are those of control systems. The tuning and refining of control circuits means that the IPMC materials could be used in reverse applications as sensors [64-66]. This offers the possibility that the actuator-humidifier material could be designed to self-regulate to a target set of values, thus saving energy and reducing complexity.

The chemistry of the sensor activity is sufficiently inert that the applications can include intimate settings such as tracheal tube flow sensors [67]. When being used in its original intended purpose application of fuel cells, the evolution of feature knowledge and methods of enhancement can be reverse-applied back into other device development such as exploiting and integrating micro-channels integrated into Nafion morphology to improve transport phenomena in humidification and motion devices [68]. Further device development along this direction has led to oscillating cantilevered beams of Ionic polymer being used for laminar mixing applications [69].

2.3 NAFION

2.3.1 HISTORY OF THE NAFION BASED IPMC MATERIAL

These polymer materials have been of research interest in fuel cells since their introduction in the late 1960's by DuPont [8, 51] and then more recently as actuators since the early 1990's [23, 63]. The ability to coat the outer surfaces of the polymer to form electrodes has meant that many new applications may be possible for these materials than were possible before. Adding motion and control of motion to the list of ionic transport characteristics means that once the scale of the phenomena and their chemistry is better understood, their inclusion in the design of medical devices and other daily use items is extremely likely.

Initially, the material was developed without certainty of purpose, because the history of Teflon development gave DuPont the opportunity to pursue research in direction based on likely benefits. This helpful direction of research has allowed for the development of a class of perfluorinated membranes that made fuel cell production possible in the mid 1960's. Now that alloying the polymer properties with metals as a polymer metal composite is possible, a whole new range of applications is being considered. To take advantage of the combination, the new applications are taking various properties from the two constituent materials of the composites and combining them to achieve new results. The scale of the phenomena and the issues to overcome mean that it is typical to think of an idea that might be possible, but then have a large number of issues to consider, address and overcome, to see if an area of application is viable or not.

In the literature review, it is evident that many groups are working on actuation and pumping of liquids with IPMC solutions. Many other groups are working on fuel cell applications [8, 24, 56, 68]. There is discussion of the movement of humidity and local atmospheric conditions within fuel cells. It can be seen in the literature that the forces from single IPMC actuators are relatively small [37], so if large volume needs to be moved, then many repetitions of small units will need to be achieved in a design and controlled to produce the needed function. If thousands of small Nafion actuation blades were needed to produce a required flow rate of air, then detecting and replacing failed blades and controlling them will be a significant development issue, but addressing that only becomes an issue if the possibility that such an adoption is feasible.

2.3.2 NAFION ACTUATION

The primary motion that was investigated for the actuation mechanism of interest was bending. Electrical stimulation of the Ionic Polymer causes the gel swelling response that enables the material to distort and move [57].

The understanding of the range of conditions, forces, frequencies and methods to control this actuation response has been extensively investigated by many researchers [13, 57, 70]. Of more than 2000 papers considered for this study, more than half involved Nafion and some form of motion.

The literature did not indicate that the proposed combined function of this study, combining electrically stimulated actuation with humidification has been considered. The conditions needed for IPMC motion, specifically persistent hydration and the effect of humidification (dehydration) are in conflict with each other, so combining the two functions involved overcoming this natural conflict.

2.3.3 NAFION WATER UPTAKE AND HYDRATION

The need to understand this aspect of Nafion's current behaviour and capabilities and the ability to improve on them is a critical part of this study. There are three areas where the extent of the water handling abilities affects other performance issues for the mechanisms of interest. In order for actuation to occur from electrical stimulation, Nafion needs to be hydrated [62].

The interface relationship with the water and air of the surrounding environment with the Nafion and electrode material needs to be characterized so that the path of water in to the Nafion for continuous hydration for actuation and the path and rate out of the Nafion for humidification can both be understood and optimised. Transmission infrared spectroscopy has been used to investigate this phenomena, so there is a method to consider the pathway and study the findings in future work [59]. The pores and channels within the polymer can be characterized and studied for specific locations of matter transport with this method of imaging as well as several others, such as contrast tapping AFM and shear force microscopy [71, 72]. The mechanisms of transport for other ions in hydrated Nafion are heavily studied for the fuel cell and sensor applications [73-75] so the capacity to isolate and confirm water transport, retention and internal changes does exist.

The effective diameter of the internal channels is in the order of 0.8 nm to 1.3 nm and the rate of water transport is affected by the extent of hydration already present. For any material condition, there will be a hydration minimum for that material where the continuity of the liquid material cannot drop below the minimum and continue to transport water. The additional issue that needed consideration and experimental design management is that once the minimum is exceeded, rehydrating the material may not be possible with the mechanism that had allowed transport only to take place. The energy of re-establishing the flow is not the same as the energy to permit flow above the minimum hydration level needed for a given flow. Reconnection of the flow pathway can be shown to hold an energy penalty when compared to uninterrupted flow [55].

The combined interactions of temperature and phase of water between liquid and vapour, as well as the atmospheric and physical pressure on the IPMC, in this case Nafion Pt, produce the exact local conditions throughout the material that determine the local and global rates of absorption for uptake, flow, transport and swelling geometry of the internal and interface molecular structures. Liquid water has a greater local effect on internal swelling and structure than the vapor and the thermal history of the material is relevant to its behaviour, but the effects are most exaggerated above 90°C Evidence exists that the initial preparation methods and conditions pre-existing affect subsequent hydration behaviour. The boiling of the raw Nafion in water has the effect of stretching and dilating the internal molecular geometry to improve the capacity of the material to uptake water and transport it in comparison to material that has never been boiled [53, 54].

The literature supports a uniform transport mechanism for protons that is independent of hydration above 46° C, but this is above the design temperature of this study, so the existence of the mechanism is important but the specifics will not be utilised for hydration or water transport, since the mechanism does not commence in the range of intended temperature operation [52]. The effect of gel swelling may be visualized in a clear gel using marker dies [76] but this technique may not be suitable for the electrode coated material of this study. Masking and selected layout design may still be able to utilise a hybrid arrangement of this imaging technique to map water motion and gel movement in the future.

Temperature has significant effects on mechanisms of transport for molecules. Fortunately, the operating temperature range of all the intended applications for this study (10° C to 50° C design and 17° C to 39° C expected real operating range) are well below the range that the first degradation band occurs for the Nafion polymer backbone at 120° C [39].

The sustained transport and modeling and confirming the persistent conditions needed to achieve this sustained state were considered in relation to the issues of cyclic load [77]. The relationship of water for hydration, humidification and actuation are intimately connected to the structure, chemistry and all the other boundary-influencing conditions of the system.

2.3.4 NAFION MECHANICAL PROPERTIES

The mechanical properties of the Nafion only were not the main focus of the study. The literature proposes many methods to measure and quantify the data of this area of work [78, 79]. The important behaviour for the mechanical actuation requirements were for the composite material. None of the intended uses were expected to be high stress for the materials, so the properties that were of primary importance, once reasonable design values were confirmed , were understanding how consistent the mechanical properties would be over time and what conditions affected these properties [72, 80, 81].

Mechanical Analysis texts for geometry, construction, motion and fluid dynamics were consulted to understand what mathematical models should be employed for basic actuation calculations and properties [82-87].

Basic material geometry was furnished from the supply company specifications [88] and then reconfirmed by manufacturer specifications and lab measurements. Long term creep and viscoelastic properties were identified in studies of similar materials as this study, so the long term behaviour could be considered as an area for future work if the feasibility of the short term behaviour established a need for further investigation [6, 89].

The structure of the hydrated material [90] and techniques to establish the geometry and characteristics of the membrane were identified to confirm assumptions if necessary [91].

2.3.5 NAFION ELECTRICAL PROPERTIES

Since the stimulation of the material is going to be achieved and determined by electrical stimulation, it was seen from the literature that understanding the electrical impedance of the overall structure and microstructure of the materials will help in understanding properties of actuation and humidification and in designing processes to modify electrical properties [61]. The state of humidification of Nafion affects its electrical properties. When exposed to air for extended periods, as the study design investigated, the electrical properties typically decay based on changes in humidification [92]. Understanding these effects and the factors that drive them was one of the intentions of the study. Another critical feature to understand the effect on electrical properties is the electrode response for Nafion [12].

2.3.6 NAFION RESPONSE DECAY

There is clear evidence that the polymer properties change with time based on how the polymer backbone behaves when hydrated and dehydrated. Several candidate materials are studied in a comparison format that reveals details about the actuation response and the decay of the response [14] It is clear that Nafion is a reasonable choice and that a good understanding of the conditions that cause polymer degradation and failure will need to be understood in the long term adoption of the materials for the study purpose [89, 90].

2.3.7 NAFION MORPHOLOGY AND MICROSTRUCTURE

The internal changes that can occur in microstructures often reveal significant information about what is causing mechanisms of the overall material. In addition understanding what scale and effects are causing microstructural changes can significantly affect how investigations are undertaken and what effects are likely to be possible or effective to produce outcomes and behaviour. One example of this concept is the water sub-diffusion in Nafion as seen at the micrometer scale in the membrane [52].

Lattice Boltzmann simulations for proton transport in 2-D model channels of Nafion also show how the protons can be moved within the existing structures and how they modify with temperature [93].

The Surface structure of Nafion in vapor and liquid also help to indicate what structures are likely, and at what scale, in the solid material [94].

2.3.8 PLATINUM DEPOSITION METHOD

The reasons to select Nafion were simplicity, appropriateness (as a typical representative material of the class being considered), availability, and processability. Since this was the thinking for the Ionic Polymer for the substrate, the same thinking was applied to the electrode coating. Processability was a key consideration in the selection of the metal and so Platinum was selected for the electrode metal and the preparation procedure was based on a method established by Millet in 1993 [95] relatively early in the research of the IPMC materials as actuators. Another very interesting modification technique that the literature revealed which was beyond the scope of this study was the concept of fabricating the electrode in a gradient [96]. The technique involved casting the Nafion material from a liquid. This was not a technique that could be undertaken with the resources available to this study, but the concept that such a method could increase the longevity of the material was important to understand for future work.

Reactive spray deposition technology was another method that could be utilised in an application once issues have been identified where the deposition technique benefits regarding porosity or bending strength justify the cost and complexity of the method [97].

A final method that has been identified as relevant to the ultimate feasibility of a commercial answer was the hybrid technique of electroplating and electroless plating [50]. This combined technique would have offered significantly improved control over coating thickness and alteration of the electrical resistance properties of resulting electrode coatings. This method was beyond the scope of this study but awareness of the technique informed the design of the experiments and is addressed in areas for further study in Chapter 5.

2.4 LITERATURE SUPPORTING A COMBINED MECHANISM

This study has been undertaken to see if the new IPMC capabilities could be combined in a suitable way for a specific medical device application: patient air humidification and air motion through pumping from a single material. The goal for this study is to consider current reported characteristics of the materials selected (Nafion and Platinum) and see if the confirmed properties could be utilised to achieve the needs of any of the current products. In a feasibility study of this type, many of the results can only be indicative of potential. The assumptions of the scale up ability of lab results and the ability to improve on lab results would have to be further investigated and defended, with additional testing before a commercial investment would be likely.

2.5 RESEARCH PLAN

In light of the literature support obtained above, the research plan for this study was to use a well-established method to produce IPMC material from Nafion and Platinum and investigate the individual characteristics of actuation and humidification of the as-produced material to quantify the characteristics of the different mechanisms. Then the novel portion of the work was to try and combine the two mechanisms simultaneously with the one material. If combination proved possible at all, it was planned to investigate if this combining modality could be improved upon for longer durations or better rate of performance. Relating the data obtained to the current commercial aspects of pumping and humidification in medical devices was also a final component of the research to determine if the feasibility was physically possible and then also commercially possible.

CHAPTER 3: METHODOLOGY

3.1 INTRODUCTION

The methods used in this investigation of feasibility were a mixture of standard procedures discussed in the literature, (such as Millet's platinum coating procedure) and new techniques developed for this research. The newly developed equipment and techniques were suggested by the evidence of the literature and preceding results of experiments that suggested a modification or development of an existing technique that would produce appropriate results. For example, if a partial result at one level of hydrostatic pressure produced a partial result, the following experiment would increase the pressure to determine if the increase in pressure sustained the first result (and revealed an exploitable mechanism), or if there was no difference. This method of development produced results that would not have been possible if all the experimental methods were only known at the start of the work. The overall purpose of the experiments was to indicate if a combined set of mechanisms could be demonstrated to achieve both humidification and actuation.

This chapter will seek to address the methods used for the following areas of work:

1. **Materials Selection** – substrate, coating and process chemicals.
2. **Preparation Techniques** – deposition methods, operating conditions.
3. **Quantification** – forces, geometry, rates, speeds, electric properties.
4. **Actuation Investigation** – all aspects of actuation effects.
5. **Humidification Investigation** – all aspects of humidification effects.
6. **Combined Humidification and Actuation Feasibility** – investigating simultaneous effects of both mechanisms at one time.

3.2 MATERIALS SELECTION

The selections and experimental design were based on best known properties from the literature. Humidification behaviour of the selected materials was based on the understanding that the intended application area would be human respiration, so the volumes and conditions of humidification were based on this expectation. Actuation behaviour of the selected materials was also based on the assumption that the conditions of the motion would be able to achieve pumping human respiration volumes of humidified air. All the conclusions of the work were based on the results of this particular set of initial choices, so the same methods could be applied to other Ionic Polymer Metal Composites, or other types of materials.

The study used standard techniques, based on the literature review, to isolate and identify mechanisms and quantify them to answer the overall feasibility question to verify a combined mechanism approach. The primary method of this study was first to identify the best candidate Ionic Polymer Metal Composite material from a literature review and then methods to transport humidity and actuate the material were investigated in individual experiments. Once the initial material properties were verified, such as humidification and actuation, then experiments were designed to investigate functional mechanisms, such as pumps and humidification delivery

Following the literature search, the selection of the actual materials to be studied was considered. This consideration included weighing such factors as availability, literature volume about the materials (amount of information readily available for study and use), suitability (for commercial use to be adopted if study findings lead to confirming feasibility), process-ability to be able to modify the materials to alter properties and behavior, physical characteristics such as density, tensile strength, flexibility and thermal and mechanical stability. All factors in any material selection process are a continuum of gathering information about a selection and then proceeding in a direction or modifying the direction to obtain a result. The literature will support what was known, but this study aimed to combine two areas of known behavior at once, so the starting point is based on likely possible outcomes.

Applying all these above criteria to the literature search data, Nafion was selected as the ionic perfluorinated polymer to use as the substrate polymer to deposit the electrode on. Nafion was the earliest commercially produced ionic polymer and as such has the most use and process information available easily. There is more microstructure and compound information about Nafion than any of the other similar materials produced by competitors of the DuPont brand. There are variations of the basic material that are commercial availability now. This clear historical leadership in the emerging fuel cell market made Nafion from DuPont a practical choice to give the research the best chance of establishing a method based on the most understood material available. In addition to the polymer constituent, there are numerous choices for the electrode deposition metal. The literature showed use of five or six metals, but platinum was chosen for its inertness and the fact that it showed less fatigue issues in the long term motion that was desired if the feasibility worked. Durability of and stability of platinum as an electrode and the lack of toxicity issues in the medical space are both important considerations in the final choice of Platinum as the electrode alloying element.

The two materials for the study have been used by other researchers, but not all the issues of interest in this study have been investigated in the behavior of the composite material where platinum and Nafion are combined. The reasons that this work has not appeared in the literature will be addressed in Chapter 5, but it is worth mentioning that there is a motion performance-limiting issue for Nafion regarding sustained hydration.

3.3 PREPARATION TECHNIQUES OF NAFION BASED IPMC

The preparation and experimental design techniques employed all had to be framed with a full awareness that there are four main areas of performance that need to be accommodated to consider the feasibility of Nafion and Platinum for an humidifying air pump application.

1. Hydration;
2. Actuation;
3. Pumping;
4. Humidification

The first area, Hydration, as has been noted, is a critical factor for all the other activities in the list. The third area, pumping, is basically a sub-category of the second area, Actuation. Effective humidification, where a rate could be measured, cannot occur without the Nafion being hydrated, but some humidification or dehydration will always occur with Nafion exposed to air. The rate might be below a measurable amount depending on contact conditions. Humidification involves hydration and Nafion actuation involves persistent hydration to sustain actuation. This means that hydration of the Nafion material is actually a central key issue to the investigation of these materials for feasibility of this considered application with humidification and actuation.

The Nafion material selected for the experiments was manufactured commercially by Alfa Aesar Ward Hill. The Nafion was nominally 0.18 mm thick material and was supplied in sheet form.

Using Millet's protocol, the Nafion was coated with platinum. In the absence of the resources to routinely inspect the detailed dimensions of all fabrication efforts, it was decided to settle on a manufacturing process for the all the coated Nafion materials and then hold the manufacturing conditions of the material as constant as possible, within the cost and inspection tolerances of the study. Throughout the write-ups that follow, all the Nafion referred to has been prepared using the procedure derived from Millet's 1993 Protocol [95] for precipitation depositing platinum on all the exposed surfaces of Nafion. Figure 3.1 outlines the two different manners in which the procedure can be utilised depending on whether all of the surface or only part of it requires Nafion platinum deposition.

3.3.1 PREPARATION - GENERAL DEPOSITION PROCEDURE

The raw Nafion material was roughened lightly with #1200 grit wet and dry sand paper then cleaned by soaking in a 1:1 solution of 1M Sodium Hydroxide (NaOH) and De-Ionised (DI) water (H_2O) distilled water (H_2O) for 1 hour with gentle warming at approximately 60° C and agitation. The pieces were then immersed in a solution of 0.01M Pt(NH4) solution for a period of 24 hours so the majority of the reaction has self-limited the surface deposition to a consistent thickness. After the deposition step the Nafion pieces were washed briefly in de-ionised water, then the platinum was reduced by immersion in NaBH4 solution for 2 hours with gentle heat (approximately 60° C) and agitation (approximately 80 RPM). Finally the now platinum-coated Nafion was actively hydrated by boiling in DI water for an hour, then rinsed with fresh DI water and patted dry with paper towels.

In order to preserve the integrity of the coating quantity and process, the solutions were renewed every month or after being used six times. The general process is outlined in the process flow chart as shown in Figure 3.1.

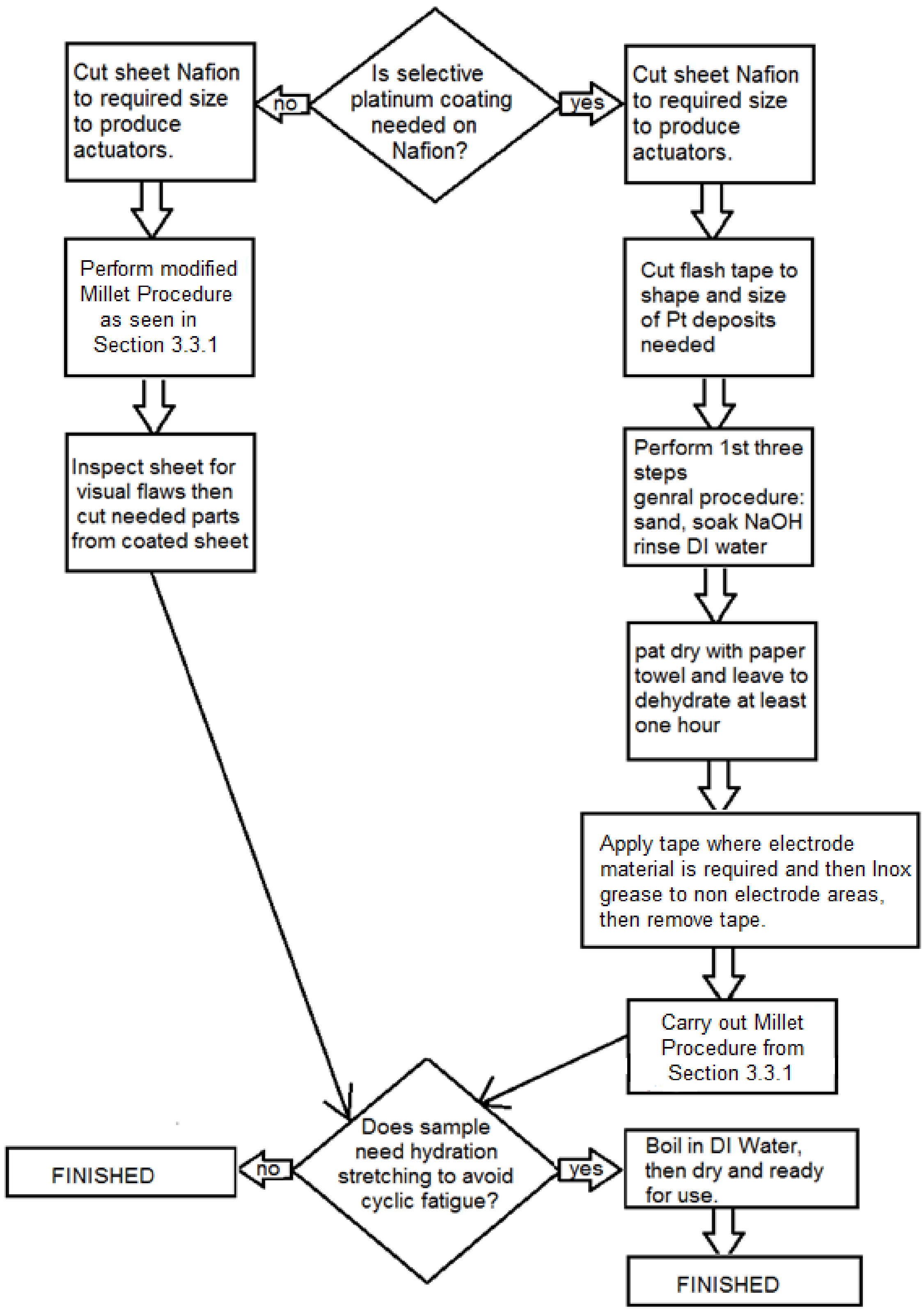


Fig. 3.1 Coating Process Flow Chart

The sheet Nafion had a tendency to float during deposition, so a glass rod or other inert mass could be positioned on the Nafion in a vessel of solution to ensure that the entire surface remained submerged for the whole deposition period. In Figure 3.2 the complete exposed surface was submerged in the depositing solution in such a manner. Once the deposition was complete, the material was no longer as buoyant and the rod was removed.

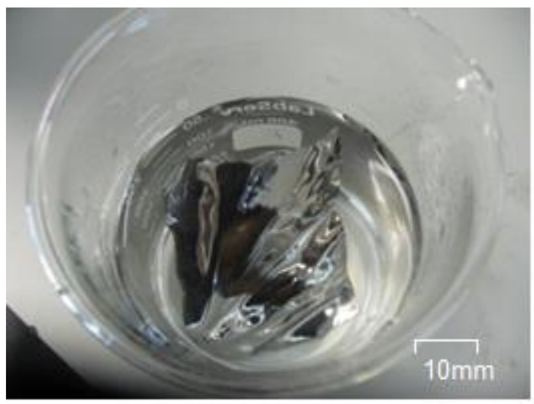


Fig. 3.2 Smooth surface appearance of Nafion being platinum coated in solution

The technique outlined in the procedures from Millet [95] yielded repeatable coatings of platinum onto all the exposed surfaces of the sheet material. Since this study was focused on feasibility, the exact thickness of the coating was not measured but an average thickness was calculated based on the assumption that the chemical deposition technique using the same materials, fresh reagents and run for the same length of time at the same temperature should produce reasonably consistent amounts of deposited material. If deposition thickness is an important factor to future applications, then some indicative microscopy should be undertaken routinely to confirm that the deposition reaction is producing even thickness of deposits and uniform structural properties in the deposited metal material.

The process appeared to be self-limiting in that the amount deposited did not significantly increase when a sample was left in the solution past the prescribed exposure time of 24 hours. One of the sample preparations was left in for more than 24 hours over a weekend for 72 hours. The increase in mass was not significantly greater (less than 10% more by weight) than the 24 hour period described in the procedure. The platinum deposited did not continue to increase and increase over the course of the extra time. The deposition amount was not varied on purpose with the factors of the preparation of the materials being kept as constant as possible. The initial technique was undertaken using a method of deposition originally developed by Millett. Once this method was confirmed as viable for producing the basic composition, some variations were undertaken to mask off regions and select deposition regions.

3.3.2 PREPARATION - VARIATION IN COATING LAYOUT

Several of the experimental designs required producing patterns of electrodes where continuity of Nafion was required, but not continuity of Platinum coating any patterns produced, where the entire surface of the Nafion was not coated with platinum, were produced by masking off portions of the surface to block the chemicals from depositing the platinum in the areas where prevention was desired. There were four masking materials as shown in Figure 3.3 trialed for their blocking effects and adhesion in process conditions:

- MX6 Inox with PTFE premium grade machinery grease distributed by Candan Industries
- Fix A Tap waterproof Lubricant
- Vinoleo WT90 waterproof lubricant
- High Temperature Mylar Flash Breaker Tape distributed by Airtech Industries

a) b) c)

Fig. 3.3 a) Grease options to test b) tape masking c) resulting Pt electrodes on sheet Nafion

3.3.3 PREPARATION - PATTERNS ON THE NAFION COATING & MASKING METHODS

The actuation investigation required the ability to form electrodes that were not completely Platinum-coated Nafion surfaces, so several techniques for masking and blocking off the platinum deposition methods onto the Nafion surface were investigated experimentally and then the techniques were judged. The most acceptable technique or, combinations of techniques, for a given purpose were employed to fabricate different electrodes for various experiments. The characteristics of one solution often provided one aspect of control that was needed over another aspect that a given technique would not allow. For example the sharp edged masking of one type of tape would not remain in-tact for the chemical sequence of the deposition, but would work to apply a crisp edge to smear grease against that would survive the chemical sequence. There was no method to apply the grease in such a straight line and no tape the study had access to that would remain in contact with the hydrated Nafion throughout the process. Combining the two masking techniques produced a usable method to form straight edged deposits of platinum on the Nafion in locations as required.

3.4 QUANTIFICATION

3.4.1 DETERMINATION OF COATING THICKNESS

The first calculation undertaken at the start of the experimentation was to determine the thickness of the coating, assuming that the deposition technique produced even distribution of the metal on the substrate surface. Using this assumption, and knowing the density of platinum and the surface area of deposition, the thickness was calculated based on the geometry shown in Figure 3.4.

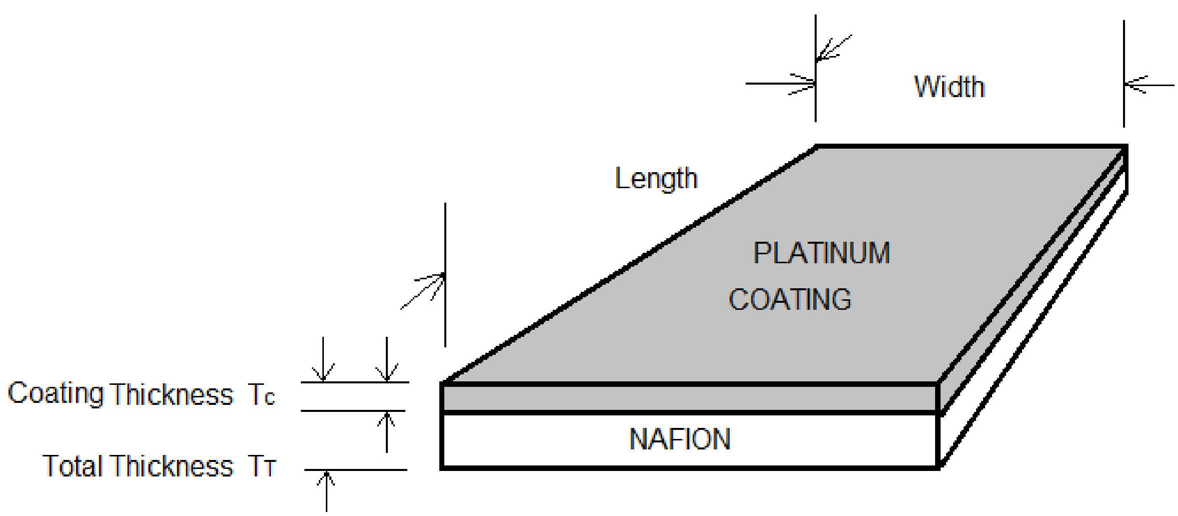


Fig. 3.4 Geometry of coating thickness calculation assumptions

3.4.2 QUANTIFICATION OF INITIAL HYDRATION

Four pieces of uncoated Nafion and four pieces of Platinum coated Nafion were weighed and measured dry. Then the same pieces were immersed in de-ionised water for 15 minutes, then removed, patted dry and weighed again within a minute of removal. The differences in mass were calculated from the data and the results reported in Chapter 4 of this study below.

3.5 INITIAL ACTUATION

This part of the investigations constituted the largest single area of focus. The methods discussed in this section were designed and adopted to try and understand what was possible, in the area of actuation, for the chosen materials that were selected for this study. The results of the earliest experiments lead to the final actuation investigations that are listed at the end of this chapter. Including the final actuation work in this section would place the outcome before the enabling discoveries that they supported. The evidence that allowed the last experiments to be designed and run was therefore presented here before the Final Actuation Section to present the evidence for the final design.

3.5.1 MOTION EXPERIMENT DESIGN

It was decided early in the experimental design to use the same electrode clip for as many of the experiments as possible, so that the attachment area could be considered roughly the same for each experiment rather than having to reconsider this issue over and over between samples. When the multiple beam / member experiments occur, the additional electrode area can be addressed, but the majority of the experiments used the same membrane – electrode interface for consistency and convenience.

The literature reports that Nafion needs to be hydrated for motion to be possible with electrical stimulation. Since the reported mechanism of the motion is rapid ionic swelling from the electrical stimulus causing proton transport internally, hydration would appear to be essential for this activity to occur. For thoroughness, to confirm this point, dry platinum coated Nafion was attached to the electrode clamp holder in three widths and a range of voltage and frequencies was applied to see if motion of dry Nafion could be obtained.

3.5.2 MOTION CONFIRMATION

The next preliminary experiment was to verify that the material produced could produce motion. A DC source of constant electrical voltage and steady current

(PowerTech MP 3035) was used to try different Voltages between 3 Volts and 12 Volts. A dry piece of Nafion-Pt sample was placed in a clamping terminal apparatus. The Nafion was as coated thickness and the cut dimensions were 10 mm x 50 mm approximately 10 mm of the 50 mm length was held in the clamping mechanism of the terminal connection jig. With the dry sample voltages of 3 Volts, 4.5 Volts, 6 Volts, 7.5 Volts, 9 Volts and 12 Volts were applied to the dry sample. No motion was observed from the sample at any of the voltages applied. The literature all suggest that up to 6 Volts should produce some form of motion in properly hydrated and metal coated Nafion.

The same piece of Nafion was placed in de-ionised water for 15 minutes to hydrate it. The earlier humidification experiments had already confirmed that the material would readily hydrate when brought into contact with water, so the 15 minutes hydration was used to guarantee that the conditions would represent well-hydrated material behaviour.

The fully hydrated Nafion-Pt sample was reinserted into the same apparatus and the same voltage settings were repeated starting at 3 Volts DC.

3.5.3 FORCE OF ACTUATION

After the dry material tests were conducted, the very first motion experiments used a small DC power supply, as shown in Figure 3.5, to confirm that the hydrated platinum coated Nafion would move when energized and to quantify the force of specific geometries. In these experiments, the actuator beam shape was a simple rectangle and all the force measurement Voltage settings were 3 Volts D.C. The beam was varied between 10 mm, 5 mm and 2.5 mm wide and between 40 mm and 22 mm in length decreasing in length by 3 mm per trial at each width. The force was measured by actuating downward on a micro-balance that was zeroed each time after beam contact was made but before the circuit was completed. The materials were rehydrated after each use since hydration had been established as important to actuation ability by the dry actuation test and the literature revue.

The other settings on the steady power source were 4.5 Volts, 6 Volts, 7.5 Volts, 9 Volts and 12 Volts. These were also tried, but the extra energy at 6 Volts and above started to degrade the surface of the material. After the proof of motion was established with our basic material, further motion verification experiments were performed using variable AC power supply Hewlett Packard 33120A 15 MHz Signal Generator and the Nafion was hydrated in a shallow petri dish of distilled water for the 15 minute period determined as the minimum for all subsequent experiments.

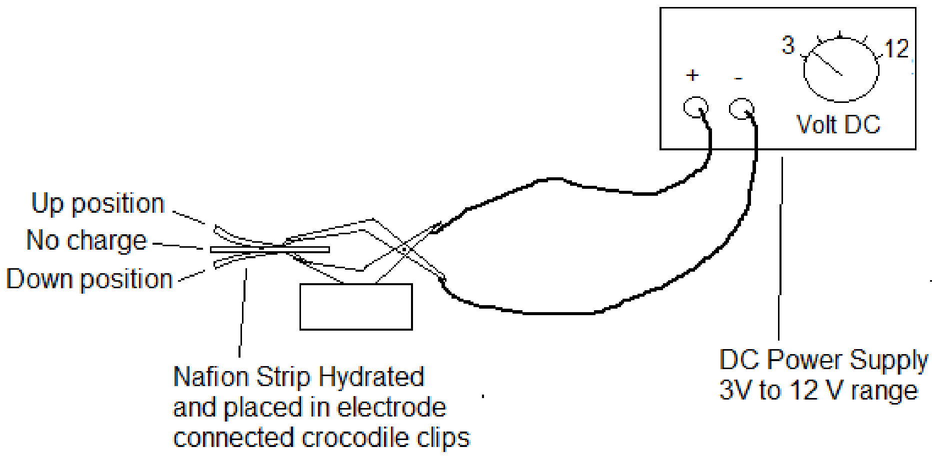


Fig. 3.5 Actuation apparatus for first actuation testing

The first detailed motion testing was hydrated strips coated on both sides, of different dimensions. The variables were length and width of the material to determine a practical “standard size” for the rest of the work and to quantify the effects of the two dimensions on the motion. Various voltages and frequencies were applied to find an excitation that would suit the shape and specific conditions of each sample. Tuning the sample to the energy supplied value was visually achieved by dialing the frequency at a known voltage until the motion deflection maximum was observed (subsequent video measurements confirmed that the maximum displacement correlated to the fastest velocity of motion). The hydration procedure was to immerse the samples in distilled water for a minimum of 15 minutes.

The quantification experiments were carried out at three widths of 10 mm, 5 mm and 2.5 mm and progressively decreasing lengths starting at 40 mm and decreasing by 5 mm steps to 25 mm. The goal of these experiments was to see if there is an effect from proportion or overall size on the motion behaviour. A range of electrical stimulation was applied to the various samples to form a base of comparison.

The frequency and speed of motion of the strips was determined using high speed video capture with a Photron High Speed Video Camera. The deflection and variation of the deflection was also able to be determined over a reasonable number of repetitions and level of accuracy.

3.5.4 PUMP CHAMBER DESIGN AND CFD MODEL - VIDEO SHAPE PROFILE

Using high speed video and a uniform grid background, the extent and shape of deflections for 10mm x 37mm Pt-Nafion beam were videoed from the side to determine a motion “shape profile” for the oscillation produced.

3.5.5 INSIDE ENCLOSURE OSCILLATION

The Nafion sheet actuation trials indicated that for this material configuration, no IPMC beam motion would produce significant diaphragm motion to produce a pumping mechanism for air. The maximum force generated by the most effective actuator in the study (1.2 mN see Figure 4.3) was three orders of magnitude smaller than the force needed to stretch Nafion (see Table 4.1 showing 11 MP as the lower break strength), so even a fully coated diaphragm would not generate the deflection or force to pump air at the volumes required for a device.

The most effective motion encountered from the stimulation is oscillating beam bending deflections. Oscillations as large as 8 mm were observed and it was decided that oscillating beam deflections would be the focus of all the mechanism investigation for the rest of the study. After oscillating beam was identified as the preferred actuation mechanism, quantifying the flow that could be achieved with a beam and addressing operating conditions of the actuation, humidification and hydration mechanisms were investigated.

A beam moving in open space would not generate flow of air in functional manner. Obviously the motion of the IPMC material through the air surrounding it produced some motion of the surrounding air, but this did not represent measurable air flow in a direction, as air moving down a tube or passageway would.

It was observed that actuating up and down, with respect to the direction of gravity, produced obvious asymmetry of motion with respect to range of deflection. Obviously, the beam mass could contribute to and extend the motion and final deflection in the downward direction and also inhibit the motion in the upward direction through the additive effect of the mass of the beam increasing the resistance to motion in the upward direction. To avoid this undesired contribution of the beam mass, the clamping fixture was rotated 90 degrees so that the beam could be oscillated left to right across the direction of the gravity field. The motion was video recorded and still images were extracted from this recording. A composite image was produced in the third image of Figure 3.6. These images were used to determine the speed of the beam motion, geometry of the profile and extent of the deflection. This information was used to design and fabricate beam enclosures to try and produce air flow from the side oriented oscillating deflection. The goal was to produce an enclosure wall profile that would interact with the oscillation motion without inhibiting the motion. It was determined through using the first cardboard prototype that the internal side wall geometry of the enclosure needed to avoid making contact with the beam.

In order to preserve as much continuity of variables as possible, the flow experiments were conducted as quickly as possible with the same IPMC beam sample being hydrated between enclosure set-up changes. The first two enclosures allowed enough clearance between the enclosure side walls and the actuation motion that there was no contact between the actuator and the side walls observed. The third set-up, which had the tightest tolerances for displacement to wall position was placed into the enclosure, set into oscillating actuation motion and observed in the enclosure before, in order to confirm that the symmetry of motion and non-contact conditions assumed for the design of the experiment were occurring. Then the flow meter was connected to the chamber and the readings were taken.

There were three geometry arrangements shown in Figure 3.7, which were investigated to try and produce measurable air flow. All three enclosure designs housed the beam in a horizontal left to right oscillation orientation. The enclosure chamber variations were a) parallel sides, b) tapering after the actuating beam and c) tapering next to the oscillating beam. Since the last option had the most chance of making contact, the enclosure was fabricated with a profile and size to avoid beam to enclosure contact. The enclosure was also made from transparent polymer so that contact or entrapment or edge sticking could be observed and corrected if it occurred.

Theoretical chamber shape was modeled in 3D CAD as seen in Figure 3.6 a) and fabricated as seen in Figure 3.6 b), based on the motion analysis from the video footage. The assumption made in the design process was that the overall shape of the chamber should not inhibit the motion of the oscillating beam (strip) but should allow the beam motion to compress the space near the walls to force air motion from the oscillating material near the two walls of the chamber. Touching the walls at any point will be a waste of energy if the contact involves any deflection or

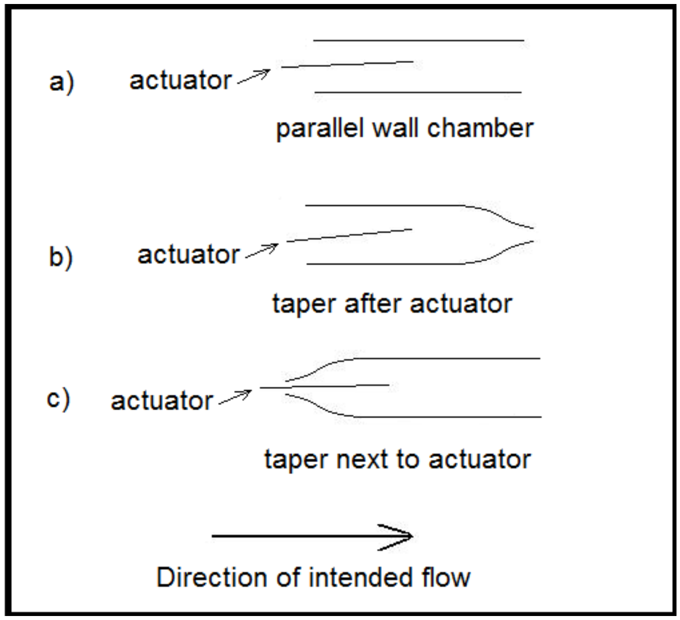


Fig. 3.6 Thee different actuator enclosure designs for the same air flow direction

compression of the beam or the chamber wall. Since this excess contact will certainly decrease the efficiency, non-contacting motion was expected and preferred for design shape priorities.

a) b) c)

Fig. 3.7 a) Chamber simulation of flow b) as built chamber c) motion of actuator tip

Chamber shapes were computer modeled in CAD as seen in Figure 3.7 so that the expected flow could be considered and modeled for the purpose of estimating flow and possible configurations of the chamber. Full aerodynamic analysis or fluid modeling was beyond the scope of this study, but the Solid Works CAD and CFD package available was utilised to consider the issues that would be relevant to a full design in future work. One diffuser was modeled, as can be seen in Figure 3.8.

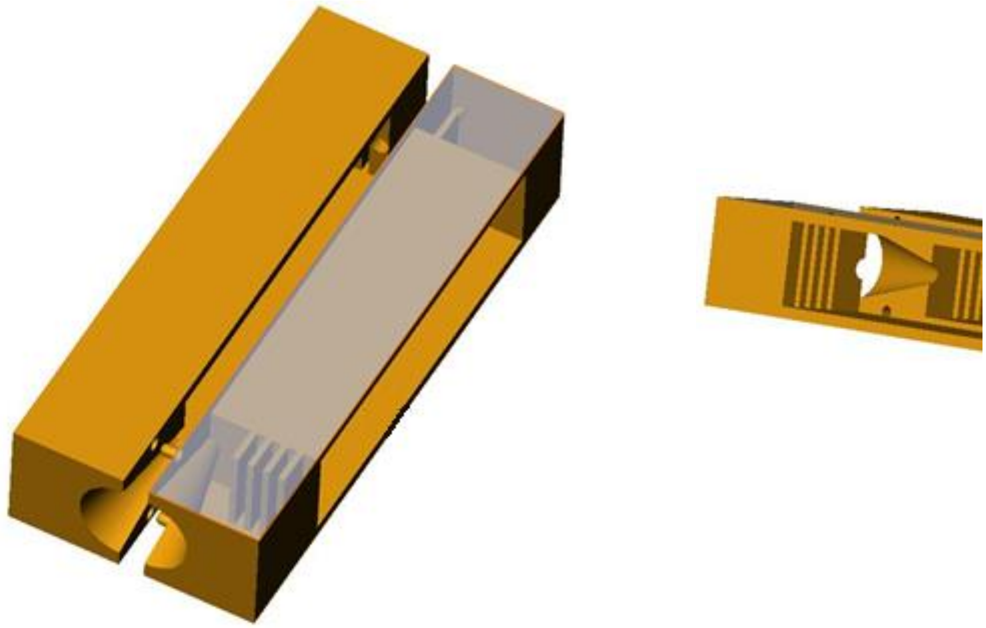


Fig. 3.8 Diffuser modeled after actuator enclosure to investigate flow

During all the experiments that were undertaken, it became clear that the hydration that took place initially to enable the IPMC to be capable of being energized and able to actuate, would decrease over a period of about fifteen minutes. The initial hydration exposure is not permanent and needs to be continued as the motion actuation occurs. The operating conditions of hydration of Nafion needed to be investigated, so that it could be determined if there is a way to extend the hydrated state and keep the operating conditions of the material in a viable state for a useful period of time.

The temperature of the entry water and the Nafion material were noted while investigating different geometry set-ups to transversely hydrate coated Nafion.

Transverse hydration failure needed to be overcome, since there is no way to use the motion technology, if permanent hydration or at least super extended hydration was not possible. The two hydration issues that needed investigation were:

1) Could transverse hydration be achieved where a water source at one point of contact can be used to supply water to stop dehydration in a different location (in this case the moving region) of an actuator material?

2) If the motion-critical hydration is possible, could it be sustained and also be used for humidification of the surrounding air environment?

The experimental design undertaken to address the first hydration persistence issue involved fabricating a double trench holder set up where two proximate reservoir "trench" slits were fabricated in a mask holder that would hold a diaphragm of Nafion with a four-beam platinum electrode pattern formed on to it. The mask holder was designed and fabricated to allow two of the trenches to be surface-filled with water next to two of the perpendicular electrodes. This would allow water to be in contact with the Nafion and electrode in two of the four-beam electrodes and two of them were connected without a source of hydration. The openings to hold distilled water were 10mm by 40 mm by 1.5 mm and were fabricated from polymer sheet material that could be flexibly clamped to the Nafion Platinum diaphragm.

Due to the shallow depth of 1 mm, the effect of pressure for the first experiments was assumed to be negligible. The next transverse hydration experiment focused on static head pressure to add energy to the desired hydration path. With a column of water delivered from a vertically mounted distilled water filled pipette, the base of the pipette was positioned directly in contact with the base of a single 10 mm by 50 mm beam of Nafion coated with platinum. The top of the pipette was loosely covered without being actively sealed. This feature was intended to minimize any water column losses from evaporation without forming a vacuum if it were fully sealed. This arrangement allowed the amount of water drawn through the set-up in a period of time to be quantified. The water consumption from transverse motion of hydration and the duration of actuation could both be observed and quantified with this set-up. The coated Nafion was pressed against the bottom edge of the pipette with the underside supported by butyl sealant tape and the upper surrounding edge of the pipette sealed against the glass and coated Nafion in the same manner. This arrangement prevented leaking water and allowed the pressure of the column to energise the contact of the water in one end of the strip and the motion could take place down the strip where the portion was free to move. The effect of pressure driven transverse hydration could be quantified and studied with this apparatus set-up.

3.5.6 PUMP MECHANISM INVESTIGATION

In order to make use of the actuation of the IPMC material for a usable pump to produce air flow, which was one of the intended purposes of the study, a viable mechanism needed to be investigated where the pumping capacity of the material could be demonstrated. Since the main purpose of this study was to identify feasible working outcomes for the material selected, several mechanisms were investigated in rapid succession. No one method was given preferred treatment, but if one method of investigation produced more suitable initial response than another, the more suitable result would be pursued instead of further investigation of the less suitable result.

The mechanisms that were initially considered were diaphragm, peristalsis, valve flap, cantilever and amplified cantilever.

All of the designs require some degree of material flexibility for the actuation to function at all. The elasticity of the Nafion material was investigated as part of the literature review and tensile testing was used to evaluate the specific tensile behaviour of the as-built material.

Nafion is not a very elastic material compared to other polymers, so it was tensile tested to quantify the amount of force needed to cause failure. The tensile strength was related to the amount of deflection possible for the material. Using the tensile and force data it was possible to investigate if a diaphragm mechanism would be suitable for further consideration. The force that could be generated by hydrated platinum coated Nafion was measured and the feasibility of the diaphragm mechanism was investigated by fabricating a diaphragm experiment, to investigate if the materials available were able to produce viable motion for a pumping application. Cantilever mechanisms of various widths and lengths were fabricated to gather force, deflection and speed of motion data about the cantilever mechanism. The presence and absence of hydration and platinum as well as different amounts of electrical stimulation were investigated with respect to the cantilever actuation mechanism.

The same elasticity, force and speed of motion issues were considered with the peristaltic mechanism and the flap valve. Since the flap valve was a variation on the cantilever, placed next to appropriate flow geometry, the data collected regarding the cantilever materials issues would be utilised in forming conclusions about viability of the flap valves well as the cantilever feasibility. The examples of flap valves succeeding in the literature are being used as pumps for a liquid and not a gas and the liquids are able to perform the hydration function as well as being the liquid being pumped. The liquid flow is also incompressible and better at maintaining momentum of motion.

Amplified cantilever mechanisms would be considered in further work, but when the issues requiring investigation for the cantilever mechanism were considered, an amplified cantilever would require all of these qualities and the ability to be increased in some respect through increased stress or speed of motion. It was determined that understanding the simpler principles of the first mechanism should be achieved, before trying to investigate enhanced but more complicated methods that employ the simpler method with enhancements.

3.5.7 A.C. VERSUS D.C.

The electrical stimulation of the IPMC materials was clearly the most practical method of delivering energy to the Pt-Nafion material to stimulate actuation. The literature reported stimulation by both types of source, so in this study, both power supplies were tested and the actuation directions, extent, ranges of motion and other side effects of application, such as damage, dehydration or mechanism decay were noted. The state of hydration of the Nafion material is a factor that will be considered and noted as the use of the different electrical signals is investigated. All actuation caused by electrical stimulation was observed to require hydration and to cause hydration to decay or cease to allow actuation to continue.

3.5.8 MULTI-BEAM ACTUATOR INVESTIGATION

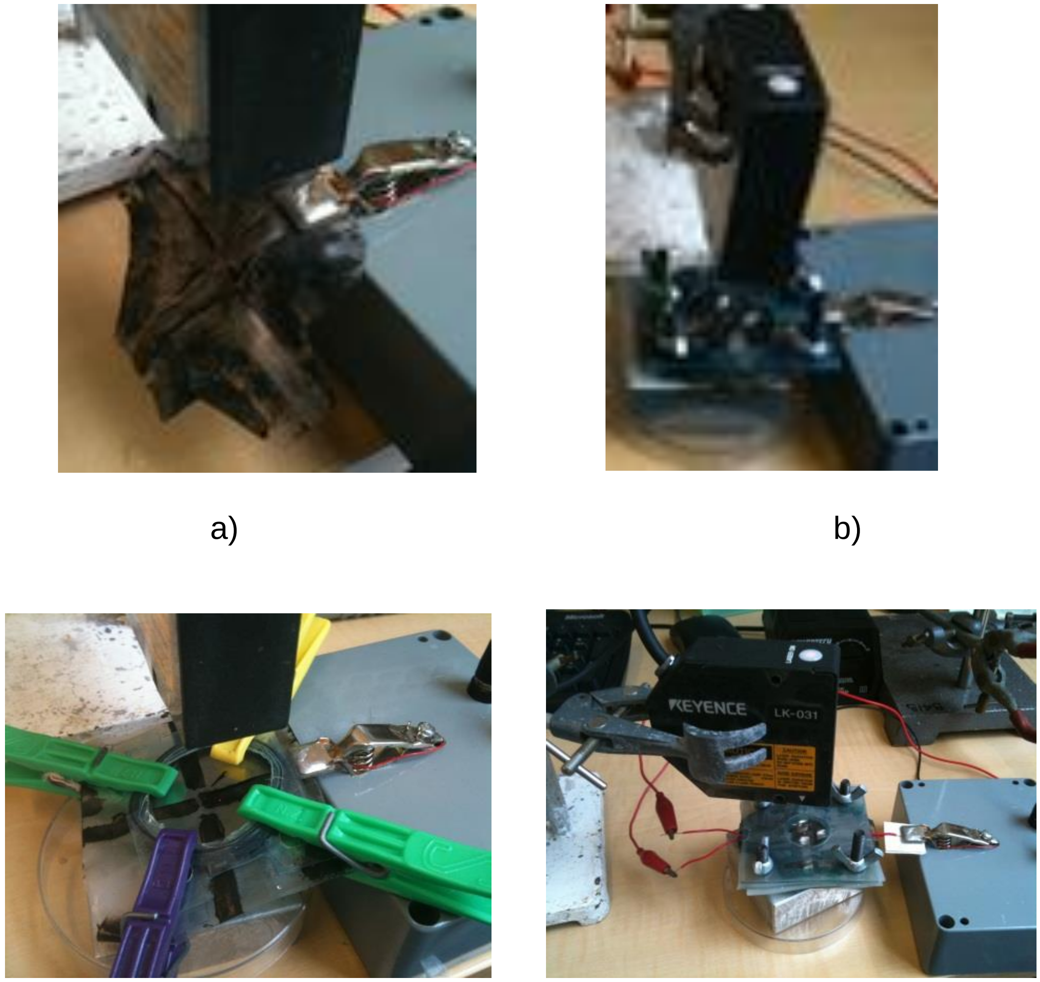
The beam geometry achieved for the sheet was approximately 34 mm x 5 mm for each of the four beams in an “X” pattern. The different restraining arrangements of the multibeam investigation can be seen in Figure 3.09. The tips of the beams were formed near each other, but not touching, to prevent a short circuit of the electrodes. The test configurations of the four beams on Nafion sheet were as follows:

a) Single beam on the sheet to confirm actuation – hydrated pre-use

b) Constrained circular openings on hard plastic above and below – hydrated pre-use

c) Rubber “O” rings added to above set up – hydrated pre-use

d) Sheet silicon with side trenches for hydration – no pre-use hydration



a) b)

c) d)

Fig. 3.09 Masked Off Electrode Actuation of Platinum and Nafion

a) unrestrained b) hard frame c) “O” ring in frame d) silicon sheet with trenches

For all the beam displacement quantification experiments a Keyence LK 031 CCD Laser displacement sensor and controller were used to measure the deflection of the material when stimulated with 3 Volts DC at 0.31 to 0.35 Amperes. The same stimulation was used for all the initial beam tests so that comparisons could be made between the different constraint and hydration effects on the IPMC material.

3.5.9 LENGTH AND WIDTH OF THE ACTUATING MATERIAL

The length and width of the electrodes were investigated to determine if there was an optimum width and length for actuation. The length and width were ranged between 20 mm and 50 mm long and 2.5 mm and 10 mm for the typical variation of width. Larger sized pieces of material could be constructed, but since the literature identified actuation samples in this size range, the materials were very expensive and time consuming to prepare, and the power mechanisms and control methods of the materials were unknowns, it was decided that manufacturing larger electrodes first would be an error of investigative strategy. If the relatively small first fabricated samples did not achieve any results, then larger electrodes could be considered as a next step for the investigations. The shape other than rectangular was not investigated in this study due to the feasibility nature of the investigation. The simplest shapes to fabricate and quantify results with were favoured for the investigation since there were so many variables to be evaluated and the shape optimization could be considered once the feasibility of double capability had first been confirmed.

3.5.10 NATURAL FREQUENCY OF OSCILLATION

The natural frequency that the IPMC beams oscillate were determined by the thickness of the Nafion, the thickness of the platinum coating, the frequency, strength and polarity of the electrical signal, the degree of hydration and the sum of the forces interacting on the materials in the system. Since this was a very large number of variables for a single outcome being considered (oscillation), the individual choices of the preparation and experimental conditions were kept as simple as possible, to observe what happened with the least amount of manipulation. For example, one thickness of Nafion only was used for all the experiments in the study. There are many listed thicknesses for the ionic polymer material, but only one was chosen for this study. One procedure for coating was trialed and adopted for all the experiments and repetition of technique was selected to produce the thicknesses of coating that were used. The natural frequency that all these variables produced for oscillating motion could be concent rated on in subsequent work, but the purpose of the initial verification work relied on making assumptions and being able to repeat the decisions in subsequent studies, where the range of variables would be further explored, if the limited variable experiments indicated a purpose.

3.5.11 FORCE OF DEFLECTION

The force that the IPMC could generate when a DC load was applied to the hydrated material was measured by applying the voltage to the hydrated platinum Nafion samples of different sizes and at different voltages. The forces were noted and the sample sizes determined for the rest of the experimental procedures of the study. The purpose of the actuation was to pump a gas, not physically move a solid object, so the oscillating nature of the actuation was determined to be of significant importance to the actuation investigation rather than the power of force that one sample could exert statically on a load sensor.

3.5.12 DEFLECTION OF OSCILLATION

The AC signal induced oscillation was considered from the point of view of deflection distance from the non-moving position (assumed to be the neutral axis of the material) and speed of motion. The frequency of the signal and what IPMC motion could be produced were investigated with optical methods such as gages and rulers as well as high speed and normal speed video and photographic methods of image capture. The effect of the magnitude of electrical stimulation (voltage) on deflection distance and the effect of continued signal while hydration decayed on oscillation was also investigated.

3.5.13 DEFLECTION

The static deflection nature of the DC signal stimulation was noted in the early experiments of the deflection extents and the decay of the deflection. It was noted how the platinum Nafion beams would actuate to a deflection point and then would often alter the position that was achieved. Since stable, repeatable actuation behaviors were the goal of the investigations, so that a mechanism could be established for humidified pumping, the results were noted as existing, but not heavily investigated. Further research might be warranted for the consistency and longevity of the AC response, but the variance was not made the focus of further study in this feasibility work.

In order to investigate the AC voltage and frequency response, hydrated pieces of 10mm, 5mm and 3 mm wide Pt-Nafion were investigated to determine what frequency and AC Voltage signal produced consistent oscillations. The method of investigation was to apply the maximum voltage first, 10 Volts, and the frequency was then moved up from 0 Hz, in 1 Hz increments to 25 Hz. When oscillation motion occurred, the maxima was noted and then the voltage was decreased to 8 Volts and 5 Volts to investigate if the maximum deflection was stimulated by the highest voltage.

A TSI 4000 Series Flow meter with a resolution of 0.01 litres per minute was connected in series downstream from the actuator enclosure assemblies as can be seen in Figure 3.10 and readings were taken from the instrument once actuation was occurring in a steady state seconds of actuation. The Pt-Nafion beam was hydrated between actuation flow readings of different enclosures, but not between individual readings for the same enclosure, set up to preserve repeatability of the positioning for the results. It was decided that moving the beams out of the set-up to rehydrate and then back into the enclosures would introduce too much variation in set-up, since the clamping position could not reliably be repeated accurately between readings.

The set-up for the flow experiments was undertaken in a shielded but not sealed system. If ambient air currents from the lab setting were not prevented, the flow rates were sufficiently low that a draft or stray air current could significantly distort the flow readings obtained for the single actuator.

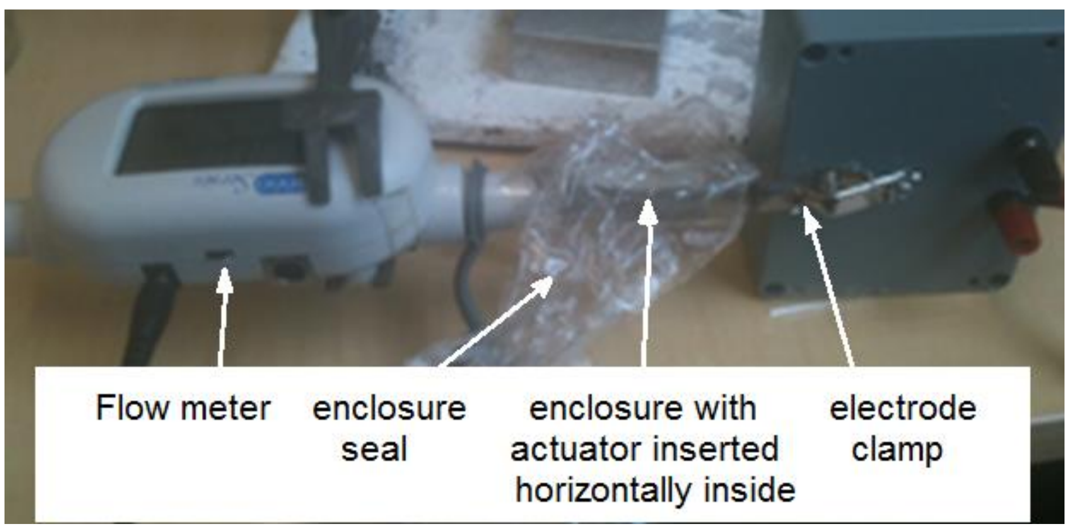


Fig 3.10 Actuation Flow Rate and Chamber Shape Investigation

3.5.14 OBSTACLES TO ACTUATION

Throughout the investigation, the methods of establishing motion were investigated and established, and then the factors that cause the mechanisms to fail or diminish in effect would be discovered and lead to an understanding of what further items would require clarification or more investigation, to overcome the obstacles. The platinum-Nafion membrane was hydrated before being stimulated to actuate. During the course of these actuation investigations, it became evident that the introduction of the hydration water from the initial exposure would last for a relatively brief period and then the effects of the hydration would decay and finally end. Typically ten minutes of “hydration state” activity was observed and then somewhere between 10 and 18 minutes into the motion, the actuation would cease. This observation led to experiments designed to make the hydration effect persistent. The ability to make hydration persistent was eventually achieved through a combination of hybrid electrode manufacture and sufficient pressurization of water delivery. The surface area of contact, orientation of the Nafion, contact pressure of the water delivery surface and position of the electrode relative to the hydrating surface all involved experimental investigation, to achieve a method that delayed hydration decay. When this extension had been achieved, the next decay period was investigated and established to exist. Further investigation would be needed to extend the decay period, but the duration achieved in the investigation period was commercially significant (24 hours) and relevant, so extension past this point was left for further study.

The literature suggested that the platinum metallic coating may work-harden. Since the actuation was seen to decay in the extent of the deflection after a period of time, it was noted that work-hardening was a possible cause of decreased deflection; however the hydration factor was also a deciding factor in limiting actuation. If a sample was re-hydrated repeatedly, the overall deflection range might become limited in range by work-hardening, but the work-hardening effect, if it was indeed work-hardening, would not cause the oscillation motion to cease, but rather just limit the range of the deflection. In order to attribute this limitation to work-hardening, the ability to measure the hardness of the platinum coating before actuation and after actuation had caused hardening would be needed. With the coating at the 1.5 to 2.5 micron range of thickness, measuring the hardness of the platinum coating was beyond the scope of the study. In addition, the focus was on feasibility and the work-hardening phenomena, if it was contributing to the mechanism decay, was not the most important issue to overcome from the feasibility perspective.

The specific stiffness of the IPMC platinum Nafion beams that were produced for the study were established by the thickness of the sheet Nafion available and the thickness of the coating that could be deposited. In this case the sheet Nafion was

0.18 mm (180 microns) and the coating was about 1.1 microns to 2 microns on each side. The stiffness available to deflect and transfer the power of the electrical stimulation into pressure, to push the air along a conduction vessel, was limited to the materials available to make the actuators and the ability of these materials to cope with electrical energy and gel swelling which the stimulation had caused. In this study, the limits were set by the necessity of making a procedure that could be achieved. In future studies where optimisation and detailed refinements of output are the focus, both the thickness of Nafion, to increase the ability to transfer power, and the thickness of platinum coating, to increase the capacity of the material to accept more electrical stimulation, without coating damage occurring, (while avoiding too much thickness to keep work hardening effects in check) will be areas where significant further investigation will be required to produce a preferred actuator design.

3.6 HUMIDIFICATION EXPERIMENTS

The literature reports that platinum coated Nafion will allow water to transport across its surface [24, 43, 44]. If water can be moved from a region of high concentration to low concentration, it would confirm that humidification can be accomplished by the material which has been produced. Confirming and quantifying the amount of transport were the main objectives of the initial humidification experiments. The experimental design investigated water transport across the membrane. The material was exposed to the flow of dry air on one side of the Nafion and a surrounding water bath with temperature control and pressure control (through depth of water immersion) on the other side of the membrane. By controlling the flow rate of the air, and the temperature of the water, and measuring the amount of humidity in the air before passing through the water bath, then measuring the humidity in the post bath air, it was possible to determine the humidification rate of the membrane at a given temperature and flow rate. Different geometries of Nafion sheet were tried. The first experiment used a tube made from coated Nafion to form part of a gas conducting piping system. The apparatus shown in Figure 3.5 was a temperature control bath with agitated temperature controlled distilled water kept at a constant temperature. The Nafion-Pt tube was surrounded by water kept at a constant temperature which thereby allowed the internal air to have a continual exposure to a source of humidification through the Nafion-Pt surface. The variables of the experiment were the cross-sectional area (CSA) of the Nafion-Pt tube, length (L) of the tube, temperature (T) of the water bath and flow rate ($\dot{Q}$). Since the tube was intended to be uniform CSA and smooth walled, the flow rate should determine the exposure of the air to the conditioning contact with the hydrated Nafion.

If the humidification aspect of the investigation went well with the tube, the idea was that the pumping could take place by constricting the walls of the tube sequentially to propel air down the structure as a mechanism of actuation to pump the air through the tube.

3.6.1 VARIABLES AFFECTING RELATIVE HUMIDITY

The variables that could be investigated for the Relative Humidity of the air flow set up are Flow Rate of the Gas (air) $\dot{Q}$, Temperature of the gas at interface **T**, Pressure of the gas at interface **P**, Relative Humidity of the gas before entering the apparatus **RH in**, Thickness of the Nafion film wet **tTLw**, and thickness of the Nafion film dry **tTLd**, thickness of the platinum coating on each side of the Nafion **tPT1** & **tPT2**, and finally area of the Nafion sheet **A**.

Some variables were more conveniently suited to vary and control than others. The flow rate of the air $\dot{Q}$ was relatively simple to control and quantify, so this was a selected variable. The temperature of the Water Bath T was easy to control so this was also selected as a variable to change and monitor. The pressure P was relatively easy to change, but the range was also slightly limited by the apparatus available (170 mm depth of tank) which can be seen in the sketch of the apparatus in Figure 3.12. Changing the **RH in** was not convenient, but measuring it was, so that was a known variable that was not chosen to be actively varied. The thickness of the Nafion could not be measured or altered easily and this was also the case for the thickness of the Platinum coating. In consideration of these variables, it was noted that they could be quantified and investigated if the default values achieved in the materials produced did not allow a result to be obtained. That is, it was assumed that if a result could be obtained with the "as produced" materials, then quantifying the effect of the specific thickness values utilised for the results, would allow further investigation of these variables to be undertaken for optimisation of the feasibility work.

3.6.2 RESULTANT HUMIDITY OUTPUT

The Relative Humidity of the air out, after passing through the apparatus, as seen in Figure 3.11, is the resultant of the above variables. This value was relatively easy to measure and was the central objective of these experimental investigations, since the humidity

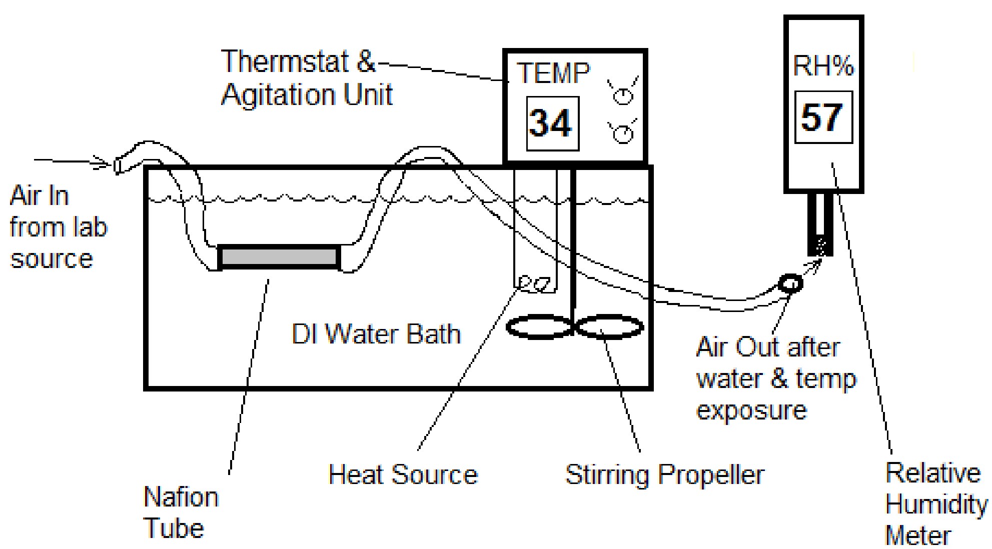


Fig. 3.11 Temperature control humidification apparatus

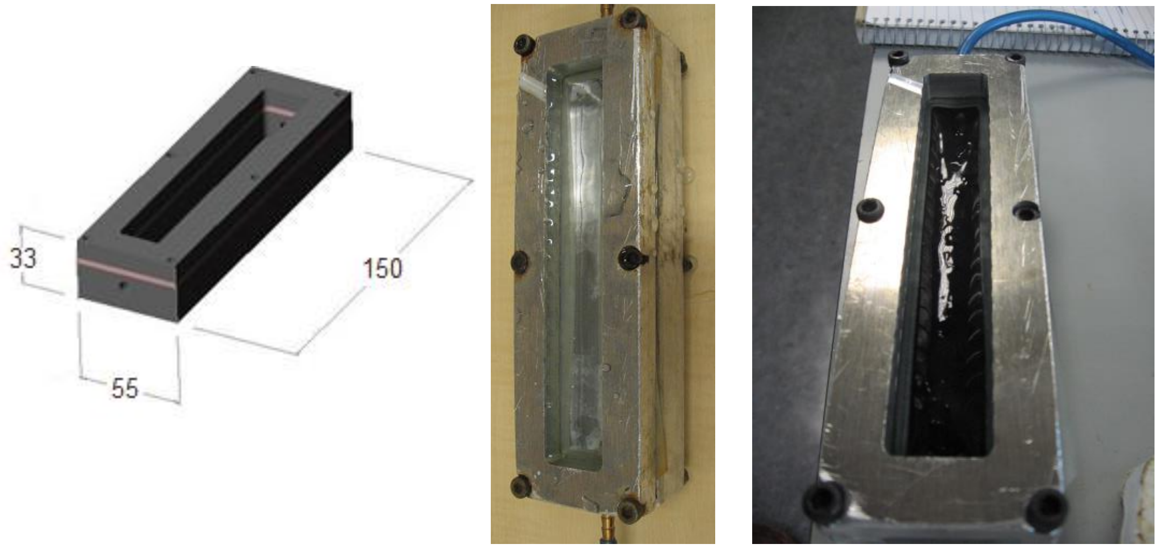
of the air delivered to a respiring human is the ultimate purpose of this portion of the work.

The thickness of coating was not specifically controlled or chosen as a variable for the study. The method to try and produce repeatable thicknesses was to hold the production methods as constant as possible so that the thickness of coating should be similar. The area of the experiments (represented by the sheet of material held in the trench holder), was held as a constant for each experiment.

The experiments were run with data being collected, but there were several problems with bonding coated Nafion to itself.as seen in the wall wrinkles in the tube design shown in Figure 3.12. When it was hydrated, Nafion swelled and changed surface characteristics and volume. When it dehydrated, these geometric and surface characteristics reversed significantly. This lead to buckling and wrinkling of the structure and the materials would frequently rupture along the adhesive line of the join of the tube. This might have been surmounted, but the tube flexure idea would always suffer from the bond line inflexibility or likely asymmetry of construction.

Fig. 3.12 Platinum coated Nafion tube for first humidification experiments

This first tube geometry problems suggested the need for a second verification test where the geometry of the material was not compromising the experimental integrity or affecting the results, so a “trench fixture” was designed and fabricated to hold sheet material in a flat position with a gas passing on one side of the sheet and the DI water in contact with the other side of the sheet at the same time. Figure 3.13 depicts the fixture as a design and the fabricated item.



a) **b)** **c)**

Fig. 3.13 Trench fixture a) Design Nafion sheet b) untreated and c) treated sheet

The trench geometry held the flat, coated Nafion in a manner where it could be moved from one height of water bath to another without touching the material or placing stress on the material that would affect its geometry. The flow rate of the gas was measured by collecting a known volume and timing the collection of that volume. This flow rate was determined in this way for all the flow rates of the experiment. The humidification of the air was measured using a Standard Instruments #SI 312 Humidity and Temperature Instrument. Initially, the exiting gas was directed at the sensor directly and it became clear that the humidity readings were heavily influenced by the surrounding air. This surround effect was mitigated by placing the sensor in the neck of a flask so that stray air motion of the room is not interfering with the air passing the sensor from experimental output.

3.6.3 OBSTACLES TO HUMIDIFICATION

The coating of platinum for the Nafion was chosen based on its inertness, availability and known processing characteristics. The humidification levels achieved in the immersion experiments and thereafter indicated that the coating with platinum actually improved the humidification ability of the IPMC rather than inhibiting it. This observed data is probably highly thickness-dependent. The relatively thin coating of platinum, compared to the thickness of the Nafion substrate appeared to allow the internal microstructure to transport water better than the Nafion natural surface on its own. It is likely that the metal charge effects were more hydrophilic with regard to water migration than the raw Nafion surface which is more hydrophobic. If the coating thickness is significantly increased, this aspect of the construction will need to be revisited. For this portion of the investigation the humidification aspects of the platinum coating process and outcomes appear to suit the needs of the study.

The speed of hydration appears to lag the function in terms of uptake and delay. There is an approximate 600 second lag between when a source of hydration becomes fully effective or the lack of hydration makes the Pt-Nafion become fully ineffective for actuation. This delay in water uptake can be further quantified if the effect becomes a long term issue for the feasibility. If the source of hydration can be made to remain continuous, then the time lag at the start of hydration is an observable fact that could be the subject of further future investigation instead of a barrier to feasibility.

The clamping pressure of the hydration source apparatus (pipette tube rim) and the electrode attachment (metal crocodile style clips) both exerted localized pressure on the surface of the Nafion or the platinum, or in some cases both. There were a range of pressures in a distribution pattern that could be quantified for both impacts, and the effects could be studied if needed. As is the case with all of these potential obstacles, the importance of investigation and determining values lies mostly in removing their effects, if they are causing a mechanism failure or such a significant rate reduction that the feasibility of the whole process is in jeopardy. In this case, both the electrode attachment clamping and the hydration contact attachment appeared to have achieved the objectives for which they were implemented. Since this is the case with both the contact methods for the primary objectives of the study, the exact values of the attachment methods forces will be left for future study. The same methods of attachment would be unlikely to be re-used in future optimization work since the horizontal slit chamber was proposed as a better hydration housing method and the actuators would be being built into the flow chamber assembly for future actuation flow investigations. The geometry, thickness and all other construction variables would be subject to review and optimisation testing in future work, so the specific clamping loads in a feasibility study to remove impediments were determined to be unnecessary.

3.7 PERSISTENT HYDRATION BACKGROUND

At the start of the experimental work, it was not understood that this section would be necessary, but during the course of actuation experiments, it became very clear that this issue of persistent hydration was a critical limiting factor to the ability to actuate and to produce a humidification effect. A method was devised to make use of all the other methods considered and observed to investigate the possibility of persistent transverse hydration.

3.7.1 INTRODUCTION

The force and pumping experiments produced evidence to make the decision to use 10 mm width as the dimension for the persistent hydration experiments. When the diaphragm experiments were run, two shallow trench slots were placed outside the metal electrode beams over uncoated Nafion regions to try surface hydration by having water on the Nafion surface next to the electrodes. The slots were 1 mm deep and approximately 5mm x 40mm and these two trenches were approximately 7mm away from each of the working electrodes on the multi electrode sheet.

The second specific persistent hydration experiment used a square polymer container 12 mm x 12 mm x 44 mm to hold a column of water. A special strip of 10 mm wide by 50 mm long of Pt-Nafion material was prepared where 40 mm of the strip was Pt coated and 10 mm was left uncoated. The uncoated portion of the strip was passed through a small slit at the bottom of the square chamber, to place it into fully surrounding contact with the water column on the uncoated surface. The full height of the water column was 43 mm when the water settled after insertion of the strip, which was 43 times more height than the first transverse hydration experiment with the side trenches on the diaphragm sheet apparatus. The platinum coated portion of the strip was connected to the electrical source just outside the chamber with a special crocodile clip that had one electrical contact on the upper side and the other contact on the lower side. Both sides were connected to the AC power source for the 10 Volt 15 Hz stimulation that the previous experiments had identified as appropriate for this study.

The method of introducing the water to the entire strip by applying head pressure to the un-coated part of the Pt-Nafion appeared to partially work. The non-hydrated IPMC material was hydrated enough to actuate for a period of time. If there had been no mechanism of hydration, then there would have been no motion at all, as had been seen with the dry samples in earlier experiments.

The next two experiments were designed to increase pressure to try see if that change could improve the duration and effectiveness of hydration and therefore the persistence of motion and also to quantify the amount of water moving through the system to consider if this method could be used for humidification.

The apparatus for the increased pressure investigation consisted of an inverted pipette tube that was arranged to press against the upper surface of the uncoated Nafion strip. The Nafion was backed on the lower side with a butyl adhesive mass (blu-tac) to allow sealing pressure of the glass pipette vessel to be applied without crushing the membrane. The balance between downward sealing force and keeping the water column from leaking out was further achieved by adding additional blu-tac around the outer edge of the glass Nafion interface after the first placement. The Nafion exposed end was placed against the full water column in the pipette tube and a Petrie dish, with the blu-tac in the centre, was then pushed onto the end of the tube. This was all inverted and the time started.

3.7.2 PERSISTENT HYDRATION MECHANISM

The presence of the water against the Nafion material in the earlier humidification experiments had shown that humidification through the membrane in the tube and flat sheet geometries was possible. Both of these humidification methods used transport pathways across the membrane from one side to the other and both worked with or without a coating of platinum. Now that actuation was involved, the pathway could not make use of a reservoir of hydrating water directly in contact with the humidifying surface. The experiment was designed to investigate if using hydraulic pressure from a static head of a column could be used to force water in contact with the Nafion in one region, to migrate through the membrane to the actuating portion of the IPMC and then continue out into the air surrounding the oscillating beam, to humidify the surrounding air.

Fig. 3.14 Pt-Nafion strip transverse hydration experiment third height version 305 mm

The electrodes were attached in the same manner as the small chamber experiment as seen in Figure 3.14. Just outside the hydration source, but on the edge of the region where the platinum coating had started. The new height was 305 mm at the start, which was a 305 fold increase over the first and more than a seven-fold increase over the partially successful “little hydration chamber” of the previous experiment. Since the water was only being exposed to one side of the material, it could be argued that the straight comparison of the two heights was not accurate. Since this was an investigation into feasibility, the exact comparison was not disputed, but each experiment was designed to suggest a "next step" rather than interchangeable results with the previous set-up.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 INTRODUCTION

In this chapter, the experimental results of the study will be reported in tables of results and figures illustrating mechanisms and plots of data. Accompanying this information will be the discussion of the points that affected the acquiring of the data, and presenting ideas and observations that affected the specific nature of the experiments. The driving goal of all the experiments was to acquire enough evidence to quantify and confirm or refute the objective question of single material feasibility of humidification and actuation.

4.2 MATERIAL PREPARATION RESULTS

Using the procedure outlined in Chapter 3 (based on Millet), Ionic Polymer Metal Composite material was formed from Nafion and Platinum. The procedure worked very well and was effective for producing consistent coatings of Platinum on the Nafion. The smoothness of the surface and the optical clarity of the surface suggested that the deposition method had achieved a relative regularity of thickness. Large variations in thickness would not allow the reflectance of the material to be as uniform in colour and direction as the coatings obtained from the preparation method. Differences in appearance between batches were attributed to the hand sanding variation in the process and the frequency of new solution renewal. These two variables could be removed with more refined processing techniques, but for a first feasibility, produced more than enough usable material for the experiments.

There were two main results from the material preparation work. The first result was that all of the surface of a piece of Nafion could be coated on both sides with a relatively even coating of Platinum. The second result was that an area or number of areas could be masked off with a tape and grease procedure to successfully coat only certain parts of a surface of the Nafion with Platinum. These results confirmed that selective deposition could be reliably achieved. The smooth and even surface characteristics of the coating process were seen in samples as illustrated in Figure 4.1.

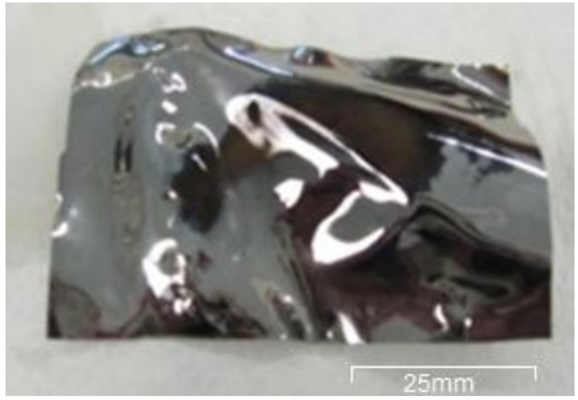


Fig. 4.1 Platinum coated Nafion smooth surface indicating even dispersion

4.3 QUANTIFICATION - THICKNESS DETERMINATION

Because the deposition method was a chemical process and there was no secondary machining process, the thickness obtained will have a range of values in any sample and across batches. The two methods that could be employed for this study, to devise a thickness value for the process were theoretical even distribution and Scanning Electron Microscope (S.E.M.) imaging, with random sample sizes and locations and statistical analysis. Since the thickness of coating and material was only needed to verify that the proportions of mechanical assumptions were reasonable, rather than a specific thickness tolerance, the theoretical value was calculated as the primary answer to the question, and then S.E.M. was used sparingly to verify that the theoretical value was reasonable for this work.

4.3.1 THEORETICAL METHOD

A rough coating thickness value in terms of average thickness was obtained by assuming even distribution of coating over the whole surface and then measuring the increase in mass before and after coating with a micro-balance. The first preparation that needed to be undertaken and verified was depositing platinum onto the entire surface of a sheet piece. Several batches of Nafion ionic polymer were coated with this technique to confirm repeatability and properties.

THICKNESS CALCULATED WITH THEORY

Volume of Platinum = mass of Platinum / Density of Platinum.

Thickness (even distribution) x Area = Volume

Therefore thickness (even distribution) = Volume / Area

This calculation method assumes that the distribution of the coating is uniform over the whole surface or both sides of the surfaces. It also assumes that the density of the coating process is uniform across the thickness of deposition. If either of these assumptions is significantly in error, then the thickness calculation of this theory could be significantly in error.

QUANTITY	VALUE
Density of Platinum =	$0.02145 g/mm^3$
Density of Nafion uncoated =	$0.00171 g/mm^3$
Sample Size 24mm x 25mm x 0.18mm =	$108.00 mm^3$
Mass of uncoated sample =	0.185g
Mass of coated sample =	0.229g
Therefore:	
Mass of Platinum deposited = 0.229-0.185 =	0.044g
$V_{\mathbf{Pt}}$ = mass / density = 0.044 / 0.02145 =	$2.066 mm^3$
Thickness (t) was given by:	
t = $V_{\mathbf{Pt}}$ / area of Nafion = $2.066 m^3$ / (24x25x2)=	0.00172 mm or
	1.72 microns

Fig 4.2 Calculation of thickness from measured data

Basic geometry was taken from the sketch in Figure 3.4. If the coating is on both sides of the material, then the area A doubles, which was accounted for in the calculation here in the eighth expression. The edges of the material are neglected for this calculation using variables shown in Figure 4.2.

The advantages of this method of thickness determination were that it was much less costly and complicated than S.E.M. It was also faster and non-destructive to the samples. S.E.M. was subsequently used to verify the theoretical thickness value determined by calculation with assumptions.

4.3.2 VERIFICATION OF THEORETICAL APPROACH USING SCANNING ELECTRON MICROSCOPE

The preparation method to produce a coating thickness, outlined in Methodology Chapter 3, was assumed to be uniform distribution. To confirm the resulting 1.72micron calculation from the methodology section, a series of Scanning Electron Micrographs were made using an Hitachi SU-70 Schottky field emission S.E.M. instrument. Based on the images, such as that seen in Figure 4.3, it was possible to conclude that the uniform distribution and self-limiting thickness reaction assumptions were reasonable. The images showed a coating thickness between 1.5 and 2.1 microns.

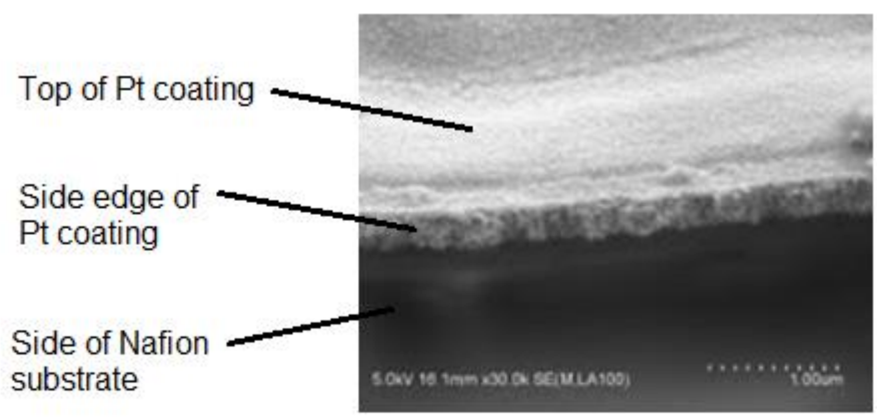


Fig. 4.3 Thickness of Platinum coating on Nafion Substrate shown in SEM image

The observed surface colour and uniformity of texture indicated a smooth surface. These visual indications of the material condition suggest that uniformity of coating thickness was a reasonable process assumption. The mass- and volume- based even dispersion calculation assumptions of the Methodology section were confirmed by the results of the S.E.M. imaging as a reasonably simple method to determine uniform deposition of Platinum on Nafion.

4.3.3 TENSILE TESTING

The Nafion and Pt-Nafion materials were both tensile-tested to verify strength and elongation values with the literature values.

Fig. 4.4 Tensile testing of uncoated Nafion

A sample of uncoated and dry Nafion being tensile-tested can be seen in Figure 4.4. In addition to un-coated and coated, the coated material was tested dry and recently hydrated. The hydration process appeared to decrease the overall tensile strength of the IPMC as built and as tested.

Table 4.1 Tensile strength of un-coated and coated Nafion

Sample	Force at break in N	Width in mm	Length in mm	Thickness in mm	Area in mm^2	Strength in Mpa
Naf only	20	10	65	0.18	1.8	11.1
Naf only	33.6	13	65	0.18	2.34	14.3
Pt-Naf dry	28	9	65	0.184	1.62	16.9
Pt-Naf wet	10	4	50	0.184	0.736	13.6
Pt-Naf dry	38.3	11	55	0.184	2.024	18.9
Pt-Naf dry	28.3	7.5	50	0.184	1.38	20.5
Pt-Naf wet	18.3	8.5	55	0.184	1.564	11.7
Pt-Naf dry	100	22	60	0.184	4.048	24.7

The un-coated and coated Nafion material was tested to determine the breaking force of the two materials. The platinum coating slightly increases the tensile strength, but the results of Table 4.1 showed that the force required to stretch the material is significant. This data confirms that using the material itself as a diaphragm material is unlikely to work well. The elongation of Nafion and the force to produce elongation is much higher than the stimulation mechanism can produce. The force per area would not allow any size reduction benefit or an energy benefit to take place from available force generation for a diaphragm design. Tensile testing of uncoated Nafion material was undertaken to verify reported tensile properties. The jaws of the tensile testing machine are intended for harder materials such as metals, but by careful loading and running of the apparatus, acceptable results were obtained. The break location of the samples occurred mostly in the intended narrowed region between the two jaws and not at the jaw edges. Breaks at the jaw edge were discarded as being uncertain results.

4.3.4 GRADIENT COATING

There were methods reported in the literature to produce gradients of coatings [50]. This manufacturing method was beyond the capabilities of this study, but if a gradient coating technique was employed, then utilization of the S.E.M. techniques to verify true deposition thicknesses and location specific gradients would be an essential tool to design and verify thickness fabrication assumptions and achievements.

4.3.5 RESULTS OF MASKING OFF TECHNIQUE

The Inox grease (blue and white tube) proved the most effective at preventing leaks and masking failures for the plating solution to be held away from the membrane surface during coating. A grease coating was able to accommodate the shift in dimensions of the 5% to 13% (increase) from the dehydrated state to the hydrated state as seen in Table 4.3. None of the tapes tested could achieve this range of dimensional adhesion and all trials resulted in delamination during process experiments. To create sharp edged regions of coated and non-coated materials with this grease, the technique of using tape to mask off the intended electrode geometry, then coating all the remaining material with grease, then removing the tape to create a clean grease free mask shaped area worked relatively well for feasibility experimentation. Improved handling, application and positioning techniques would be needed for more intimate or complex patterns.

4.4 INVESTIGATION RESULTS OF PRIMARY FUNCTIONS: HYDRATION, ACTUATION AND HUMIDIFICATION

Now that the physical quantification has been reported, the results that will now be discussed are from the experiments which showed that many factors of material and mechanical behaviour of the Nafion IPMC are often interrelated with moisture in the form of hydration. The experimental results that revealed a need for further separating of multiple mechanisms lead to the design of experiments where the various issues such as extent and method of hydration could be isolated and investigated systematically, item by item.

4.4.1 RESULTS OF INITIAL HYDRATION MASS CHANGE

The four pieces of uncoated and platinum coated Nafion were weighed before and after hydration as described in the methodology section and the results below in

Table 4.2 show that both uncoated and coated samples can hydrate and also indicates that possible contamination may affect the rate of water uptake. Sample 2 uncoated appears to weigh more than two of the other samples, and yet it has the lowest surface area. Sample 1 of the coated material has the highest surface area and the lowest absorption, also suggesting that there is some form of contamination of the material. The typical absorption shows a range of 11 to 19 percent so a design value was chosen at 19 percent to make all assumptions of design conservative.

4.4.2 RESULTS OF DIMENSION CHANGES FROM HYDRATION TESTS

In addition to the mass change from hydration, significant dimensional changes were suspected from the effects of hydration. The masking off experiments resulted in tape falling off the Nafion mid-process and the adhesive bond lines failing suggested relatively large dimensional changes through the hydration process. The results of the hydration dimensional changes investigation are summarised in Table 4.2 and show that there was a significant change in

Table 4.2 Changes in sample dimensions due to hydration swelling (all lengths in mm)

sample	DRY			HYDRATED			% change		
	Length	Width	Thickness	Length	Width	Thickness	Length	Width	Thickness
uncoat 1	65	64	0.15	66	65	0.16	1.5%	1.6%	6.7%
uncoat 2	77	64	0.15	82	69	0.17	6.5%	7.8%	13.3%
uncoat 3	77	17	0.18	83	19	0.2	7.8%	11.8%	11.1%
coated 1	120	34	0.17	122	35	0.18	1.7%	2.9%	5.9%
coated 2	35	12	0.17	39	13	0.19	11.4%	8.3%	11.8%
coated 3	24	24	0.18	25.5	26	0.19	6.3%	8.3%	5.6%

dimensions in all three directions. The design effects of this swelling were accounted for in the experimental design of the rest of the study and will have to be accommodated in any future developments.

Hydration, actuation, and humidity transfer confirmation were the first three critical issues to be investigated by simple verification experiments. Confirming that the material, as prepared, could transfer humidity across its surface and be stimulated to move were essential to confirm that the coating techniques used produced material that behaved as the literature reported. Both of these functions, humidification and actuation, can only occur if the material hydrates sufficiently, so later refinements of these two experimental areas produced quantification of the range of the humidity that could be transferred and the range, frequency and force of motion. The first results were purely confirmation that each area could be observed with the as-built material.

Table 4.3 Mass change from hydration of uncoated and coated Nafion samples

sample	mass (in grams) dry	wet	change %	area mm^2	g water/cm^2
uncoat 1	0.07	0.078	11.429	77	0.0104
uncoat 2	0.067	0.072	7.463	55	0.0091
uncoat 3	0.056	0.065	16.071	72	0.0125
uncoat 4	0.059	0.062	5.085	72	0.0042
average			10.012		0.0091
coat 1	0.033	0.034	3.030	231	0.0004
coat 2	0.021	0.024	14.286	198	0.0015
coat 3	0.026	0.031	19.231	168	0.0030
coat 4	0.026	0.03	15.385	160	0.0025
average			12.983		0.0019

The increase in mass of all the samples seen in Table 4.3 shows that hydration absolutely occurs for uncoated and Platinum coated Nafion. Knowing that both uncoated and coated materials absorb water and that the range is approximately 5 to 20 percent by mass, was sufficient information to continue with the material preparation method and the investigation.

4.5 RESULTS OF ACTUATION

All of the different aspects of actuation are reported in this section.

4.5.1 CONFIRMATION OF DEFLECTION

The Pt-Nafion strip deflected downward to a maximum distance that varied with the amount of Voltage applied as seen in Table 4.4. If the poles of the electrodes

were reversed, the direction of the motion reversed to upward. In the 7.5 Volts, 9 Volts and 12 Volts settings, the voltage was too great for the material integrity and produced thermal breakdown of the material surface. There was an audible fizzing sound and bubbling of the surface metal coating and breakdown of the ionic polymer substrate. Slight distortion of the substrate was noticeable at 6 Volts, but the material did not decay to the point of failure at this setting.

The different settings were tried in relatively quick succession, but the results for the last three voltage settings could be the result of damage to the material Some voltage value near 6V appeared to be the largest Potential Difference that this as-built material could accommodate and remain intact for a sustained period without damage occurring. Deflections occurred at the higher settings, but the material was being damaged as the movement took place, so the readings were not sustained or steady. The “recovery” of the material after the 7.5 V setting was not consistent and the material was being overloaded by the stimulation energy.

Table 4.4 Hydrated Pt-Nafion Motion Initial DC Verification of Actuation Direction Relative to Polarity and Extent Based on Voltage

V	-ve connection downward deflection	+ ve connection upward deflection
3	3	2
4.5	4	3
6	5	3
7.5	7 then twitched	5 then 4
9	6 not steady	6 then wavered and bubbled
12	8 not steady	4 then bubbled

These results confirmed that the “as built” material was able to move and maintain or alter position based on electrical stimulation as can be seen in Table 4.4. With these two results preliminary findings of humidification and motion confirmed, it is clear that the literature reporting was accurate that the materials could be assembled as described by Millet and could be conditioned with water to humidify air and could be made to move by electrical stimulation when hydrated.

4.5.2 ACTUATION RANGE

The initial trial experiments showed that DC voltage produced motion and that hydration of the material was essential to the motion mechanism continuing. Dry Pt-Nafion did not actuate and running the actuation stimulation on a single sample would display decayed performance after seven to 10 minutes of stimulation.

Persistent hydration was identified as a critical design issue that would need a viable mechanism to make this IPMC material a possible solution for future work.

The first quantification experiment to refine this data involved quantifying forces produced by the hydrated Pt-Nafion composite and relating size of the electrode sample to the force. The literature and the needs of robust mechanism design also suggested that investigating a method of electrode pattern manufacturing could be a necessity to be able to produce optimised designs.

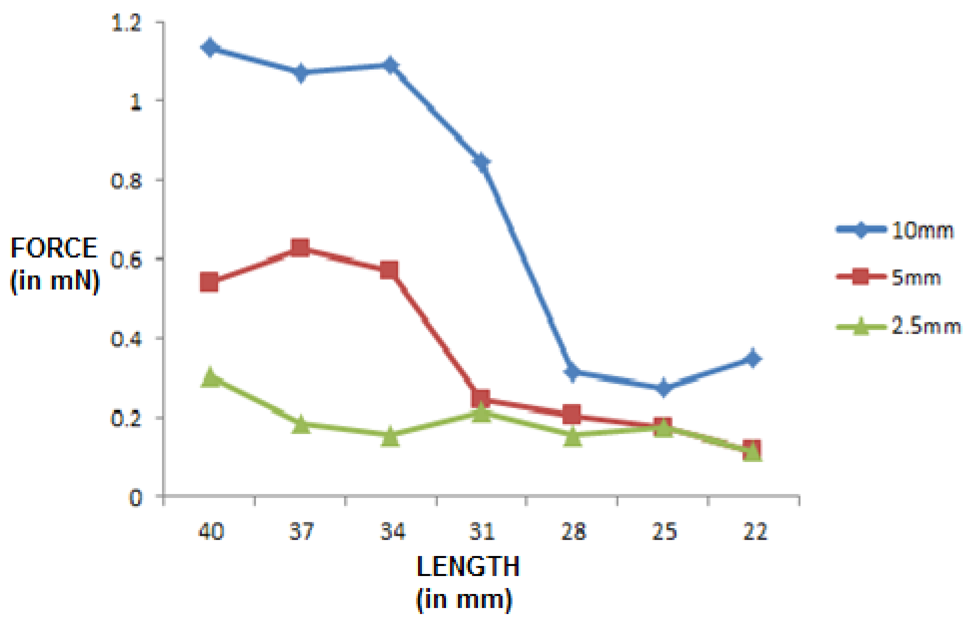


Fig 4.5 Force of IPMC against Length at constant Voltage for three sample widths

In this experiment, the actuator beam shape was a simple rectangle and all the voltage settings were 3 Volts D.C. The beam width was varied between 10 mm, 5 mm and 2.5 mm wide and between 40 mm and 22 mm in length decreasing in length by 3 mm per trial at each width. The force was measured by actuating downward on a micro-balance that was zeroed each time after beam contact was made but before the circuit was completed. The materials were rehydrated after each use since hydration had been established as important to actuation ability by the dry actuation test and the literature revue.

The results in Figure 4.5 showed that the greatest width and length produced the most force. Given the geometry of the experiment, these results confirmed that if power was the driver for a four beam and membrane design, then length should be maximized for a cantilevered beam and width should be maximised as well for the same voltage applied. Larger areas of actuator might require more hydration to remain functional. The size of the beams was selected for similarity to the literature and convenience of manufacture for available equipment as can be seen from Figure 4.6.

Fig 4.6 Nafion beam samples and DC source, fixture and scale for force

Having developed the masking off techniques to produce multiple beam deposits on a single sheet of Nafion, and quantified the force that a single beam can produce when unconstrained, the next experiment was designed to try and simultaneously actuate multiple beams on the same sheet of Nafion to make the sheet behave as a diaphragm with coordinated motion.

The first three experimental set ups labeled a), b) and c1), c2), as seen in Table 4.5, used Pt-Nafion sheet that was hydrated before testing. The first experiment a) was just used to confirm that the material would actuate when the electrode was only formed on the surfaces and not the edges of the electrode. Earlier electrodes had been formed by cutting strips from coated material, but the edges being coated was not monitored or confirmed, so the first experiment was performed to confirm that edge coating is not necessary for the actuation stimulation to take place with the electrodes on the major surfaces only, without edge metal connection.

The last experiment d) in this series was to investigate if “edge” hydration could be undertaken by placing water on the surface of the Nafion sheet in one location and having the water hydrate an adjacent region effectively enough to allow actuation to occur and remain viable. Since it had been clearly observed that sufficient hydration is needed for IPMC actuation to occur and continued actuation to occur.

Table 4.5 Four Beam sheet deflection characterisations

	DEFLECTIONS in mm		In Fixture % of unrestrained
	In Fixture	Out of Fixture	
a)	--	0.22	--
b)	0	0.08 in 30 seconds	--
	0.01	0.11 in 30 seconds	9.1%
	0	0	--
	0	1.84 in 150 seconds	--
c1)	0	0.08	--
	0.09	0.3	30%
	0.02	0.1	20%
	0	0.11	--
c2)	0.01	0.1	10%
	0.01	0.02	50%
	0.06	0.15	40%
	fail	fail	--
d)	0	--	--
	0	--	--
	0	--	--
	0	--	--

There was an important distinction to be made about water content in Nafion material. This distinction was between dehydrated Nafion where water had been actively removed from the material and "un-hydrated" Nafion where the material, in whatever state of water content it was in, did not have more water added to it. If a sample was nearly hydrated enough to allow actuation and then the water level just fell below the quantity needed, then the amount of water and the energy needed to put the water in the right part of the material for actuation would be significantly less than a piece of the material that had never had water on it or been actively dehydrated first. The literature reports that Nafion, that was boiled before being prepared for platinum coating, was capable of significantly more hydration than un-boiled material. This process history information was considered when designing the experiments for the actuation and hydration portion of the study

In order to determine practical chamber enclosure dimensions, still images were ta ken from video footage shot at high speed as shown in Figure 4.7.

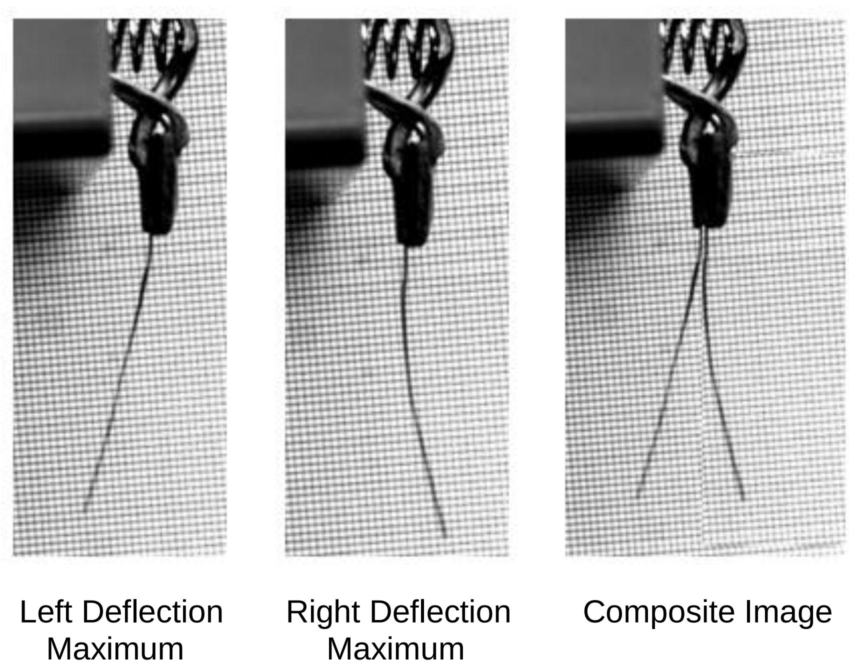


Fig. 4.7 Video of Maximum Left and Right Pt-Nafion deflections and compound image of both

The maximum deflection to the left and right was obtained by measuring the number of 1mm squares between the extreme deflections from stills taken from the high speed video footage. The images in Figure 3.6 show the total deflection(c), from left (a) to right (b), was about 14 mm and the shape from the video stills was used to design the enclosure for the flow experiments.

4.5.3 AIR FLOW VOLUME RESULTS

The air flow speeds predicted for the actuation in a chamber were modeled using the CFD package available in Solid Works, as outlined in the methodology of Chapter 3. Speeds of 5 to 11mm per second were suggested by the simulation as seen in Figure 4.8. Then the actual measurements were made of a chamber built to the design that was simulated. The simulation units were mm per second of individual particle motions, whereas the measured units were litres (volume) of flow per minute (unit time). Since the area of flow that the CAD simulation used for the calculation of speed is not known, it is not possible to compare the results for accuracy of modeling, but both results indicate that flow was possible with the mechanism and chamber shape that was considered. Based on the experimental set-ups discussed in the methodology section, the flow readings were taken and produced the following results shown in Table 4.6. The flow rates were very low, but this was expected from the CFD simulations for a single

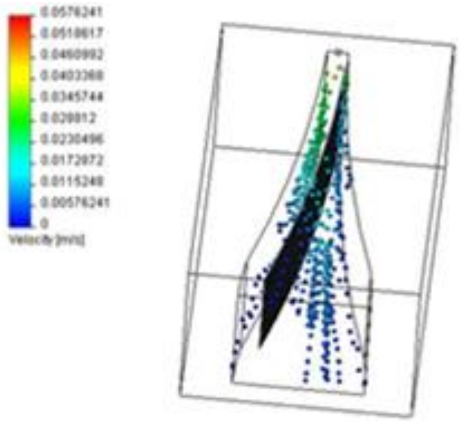


Fig 4.8 Air flow speed CFD 2D model output

actuator. Quantities of actuators likely to be needed in a real application are discussed in the Future Work section of Chapter 5.

Table 4.6 Flow rate measurements for different actuator enclosures in litres per minute

Flow reading #	a) Parallel Sides after Actuator	b) Taper In (narrows) after Actuator	c) Taper Out (widens)next to Actuator
F1	0	0	0.02
F2	0	0	0.05
F3	0	0	0.03

The results of these three flow measurements showed that the same energizing of the same Pt-Nafion beam with fresh hydration produced no measurable flow in the parallel enclosure and in the narrowing enclosure. This does not mean that there was absolutely no flow; just that the flow produced was below the scale of the instrument available. Both the first and second enclosures produced a flow that the skin on the back of the hand could feel. This flow was below the 0.01 litres per minute that the flow meter could resolve. The enclosures both focused the actuation enough to produce some detectable air movement.

In the chamber where the actuation was positioned near to walls that approximated the shape of the actuation, a flow could be measured. The average flow from this set up was 0.033 litres per minute. If this flow rate was assumed to be reasonable, if inefficient, then from a pumping perspective, to obtain a flow rate of 6 litres per minute, if individual beam throughputs were additive, then, if the lowest flow value measured were used, at least 50 beams per litre per minute flow required or 300 actuators in total might be capable of producing the desired 6 litres per minute in a device setting.

In Chapter 5, theoretical designs for layouts that could adopt these results were discussed. Also factors such as decay of response, excess capacity need (higher top throughput), range of variation and speed of flow rather than volume of flow were all items that were addressed in regard to the geometry and application needs. In the “Items for further study” section, the detail of some alternatives were presented for consideration.

4.5.4 ALTERNATING CURRENT POTENTIAL DIFFERENCE SIGNALS

It was identified that the stimulation source should be an AC voltage source with frequency control to stimulate the IPMC to oscillate rather than just deflect in one single direction. The frequency control allowed the fine tuning of the response to be optimised relative to the motion required. The unit used for all the AC investigation work was the Hewlett Packard 33120A 15MHz Signal Generator. Precise control was possible as can be seen from the readout depicted in Figure 4.9.

Fig. 4.9 Alternating Current Voltage Processor

4.5.5 ELECTRICAL STIMULATION

The D.C. stimulation of the samples only produced a deflection response in one direction that could increase in magnitude and then often decayed to a lesser deflection, but it did not produce oscillating motion. Through the D.C. investigation it was shown that a pole reversal would drive a given deflection in the opposite direction. This suggested that alternating current would be likely to produce deflections in two directions for a given IPMC such as the Pt-Nafion of the study.

For a given geometry, it was assumed that there was a best excitation potential difference and frequency of excitation to produce the most effective oscillations for air movement. It was investigated to determine what voltage and frequency were the best for this material in these experimental conditions.

The literature and initial DC experimental work had suggested that the frequency would be below 10 Hz and the voltage would be less than 5 Volts. However, the harmful effects of persistent current in a DC source was not causing the same damaging response to the IPMC with the alternating source, so values outside this range were explored.

Experimental investigation revealed that larger applied voltage produced greater deflection, with all other conditions held constant. The frequency of the source was important to the onset of a deflection response. By applying a voltage and alternating the frequency of the source, values where deflection oscillations would take place were recorded as seen in Table 4.7.

Table 4.7 Voltage and frequency selection for Persistent Hydration experiments

width in mm	**frequency** in Hz	**oscillation max in mm**
10	13	1.39
	14	1.41
	15	1.49
	16	1.47
	17	1.46
5	6	1.09
	7	1.26
	8	1.13
3	15	1.13
	16	1.44
	17	1.23

The results showed a frequency range between 13 and 17 Hz where the 10 mm wide stripe consistently oscillated distinctly. It may have been a resonant frequency, but it was not repeated at 26 Hz to 34 Hz, so the lack of repetition at any multiple of the first response frequency made it an unusual resonance since it did not repeat. No other frequency produced the motion seen at this threshold. It was observed that the larger the voltage value, the greater the deflection. At 10 Volts, the motion was the greatest. The 5mm strip had a lower frequency max of

7 Hz and the 3 mm strip had a maximum oscillation response at 16 Hz.

For all the experiments, running the oscillation set up for more than six minutes without fresh hydration was not consistently possible. After ten minutes, none of the samples were running at a visually distinguishable deflection. A series of experiments were designed to see if there could be a way to make hydration of the material continue past the ten minute duration barrier that had been noticed during the oscillation experiments.

4.6 HUMIDIFICATION RESULTS FOR CAPACITY

For the humidification phenomenon, the first next step was to investigate the humidification capacity, while removing the geometry issues experienced by the tube construction. The actuation mechanism was not suited to the behaviour of the material. The tube geometry did not allow the material to distort in a contracting manner that could produce gas motion. Uniform hoop contraction and sequential axial propagation were beyond the fabrication and measurement scope of this study, but the evidence of the experiments suggested that the time scale, motion range and repeatability would not be sufficient to construct an annular actuation design that could move sufficient volume of air and remain functional and hydrated for an actual application, at the scale of human needs (e.g. at least 6 litres per minute of air volume and starting at relative humidity of at least 50% humidification). The degree of motion for the tube geometry (deflection amount) and the direction uniformity did not produce a response that would propel air in a given direction, or at a significant or even measurable rate. No visually observable motion was detected for the Pt-Nafion tube, and once the hydration volume changes caused the seam splitting, further property investigation was not undertaken. Since the fabrication methods, material variations (thickness of uncoated sheet) and coating thickness determination and control (thickness and evenness of coating) available were inadequate to investigate accurate tube constriction designs, it was decided to investigate the flat sheet edge constrained hydration properties to determine the hydration properties. The flat sheet mode had better motion property options for combining functions, where working humidification and a method of actuating might be able to be combined as one multi-purpose material actuator.

4.6.1 TRENCH FIXTURE HUMIDIFICATION EXPERIMENTS

The first trench experiments held the flow rate and temperature constant to see the effect on Relative Humidity. Table 4.8 showed that the same five minute humidification exposure produced significant increases in relative humidity for both experiments, with an increase in the relative humidity of the exiting air of

35.7% and 34% respectively. This experiment confirms that within the range of temperature of interest for feasibility, 20°C to 45°C, the membrane was capable of passing on humidity to air and significantly humidifying it at a fixed flow rate.

The variables that were used to investigated relative humidity with the "trench fixture" were shown in Figure 4.10

$\dot{\mathbf{Q}}$ - Flow Rate of gas (air) (in litres / minute).

T - Temperature of surrounding water bath (in degrees Celsius).

P - Pressure determined by measuring depth of water D to vary pressure on the membrane (in Pascal).

A - The Area exposed to water was constant at 22 mm x 145 mm = **3190 mm^2**.

Fig. 4.10 Variables used for Humidification Experiments

As a control, some of the experiments were conducted on uncoated Nafion to see if the Platinum coating was inhibiting humidity transport across the membrane. Within the error of the experimental measurements, the platinum coating did not appear to alter the rate of humidification of the exiting air.

4.6.2 TEMPERATURE AND PRESSURE EFFECTS ON FLOW

The rectangular cross sectional area of the trench fixture was operated was operated at different surrounding temperatures and the depth of water in which the water bath surrounded the membrane was used to vary the pressure for different known flow rates.

Table 4.8 Relative humidity at constant flow and temperature

Test number	Time min	Q litre/min	Temp Water Bath °C	RH out %
1	0 5	2 2	30 30	52.3 88
2	0 5	2 2	45 45	58 92

The next experimental set-up varied the flow rate and held the temperature constant. The flow rate was set to a maximum value of 6 litres per minute (the theoretical design value of an application) and the chamber was just submerged in the water bath apparatus with the temperature control set at a constant of 20 degrees. The purpose of this experiment was to understand what effect the flow rate would have on Relative Humidity of exiting air. There was a clear inverse relationship between the contact time, determined by flow rate, and the humidification that occurred. Faster flow allowed less humidification to occur than slower flow, as can be seen from the graph in Figure 4.8.

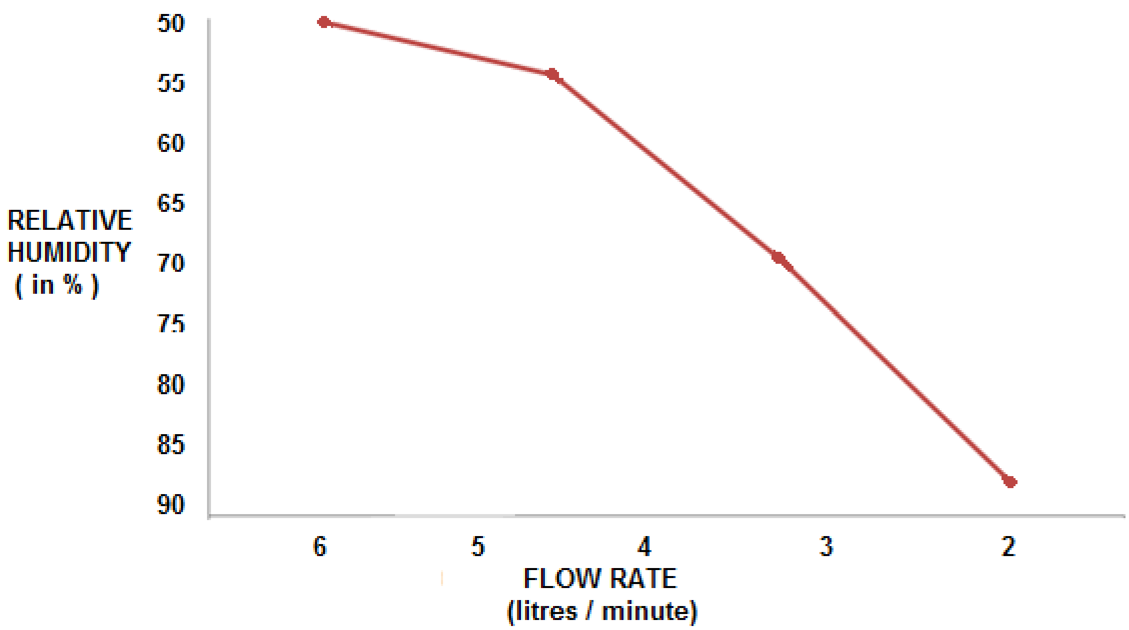


Fig. 4.11 Relative Humidity of Exit Air versus Flow Rate

From the data shown in Figure 4.11, it is clear that the rate of volume flow affects the amount of transfer of moisture through the membrane and thus the relative humidity achieved in the exit gas. Producing a flow rate as slow as 2 litres per minute achieves a high relative humidity reading of 87%, while at the same temperature, with the same contact area A, a flow rate of 6 litres per minute only produced 50% relative humidity.

These results were used to consider the design issue of what surface area of material would need to be selected, if a known flow volume and humidification rate were needed for a particular application. Typically a flow rate of 6 litres per minute would be a standard adult value for design purposes, so if the flow rate needs to be that amount or more, the area of contact to achieve the needed moisture content can be varied to achieve the needed target. These values were important in establishing that the material could achieve the needed humidification.

The final verification of a factor that might affect humidity transfer through the coated membrane was pressure. Two experiments were conducted where the flow rate, $\dot{Q}$, was varied in a series of rates. One series was conducted with the membrane at a depth of 135 mm below the surface and the other was conducted with the membrane only 10mm below the surface. Since:

$P = \rho \times g \times h$

and ρ water is 1000 kg / m^3 g = 9.81m / s^2 and h = 0.135m

P135 is 132.4 Pa and P10 is 9.81 Pa

.

Table 4.09 Flow rate, Temperature and Relative Humidity at 135mm depth H2O immersion

Q air l/min	T water °C	RH air out %
7.2	17	48.7
5.4	17	50.5
4.8	17	52.3
4.2	17	53.5
3.6	17	54.6
2.4	17	58.4
1.2	17	62.1

Table 4.9 and 4.10 show the results of experiments where similar flow rates were used at constant temperature but with different amounts of pressure

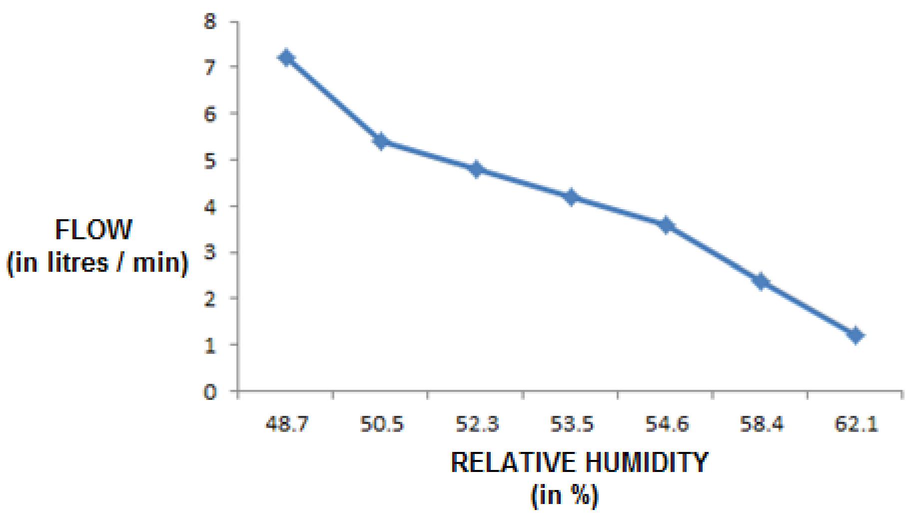


Fig. 4.12 Flow rate versus relative humidity at 135mm depth H2O immersion

The experiments produced different amounts of relative humidification. These results are graphed in Figure 4.11 and Figure 4.12. The graphs show that the trend of flow against percentage change is similar but that the increased pressure does increase the overall amount of relative humidity achieved. This showed that pressure could be used to increase humidification as seen in Figure 4.13.

Table 4.10 Flow rate, Temperature and Relative Humidity at 10 mm depth H_2O immersion

Q air l/min	T water °C	RH air out %
7.2	17	38.4
5.4	17	40.8
1.2	17	51.6

The data produced the same form of curve showing that decreased flow rate leads to increased relative humidity output suggesting that at the same temperature, increased contact time with the humidifying surface increases the relative humidity of the gas coming into contact with the humidifying surface.

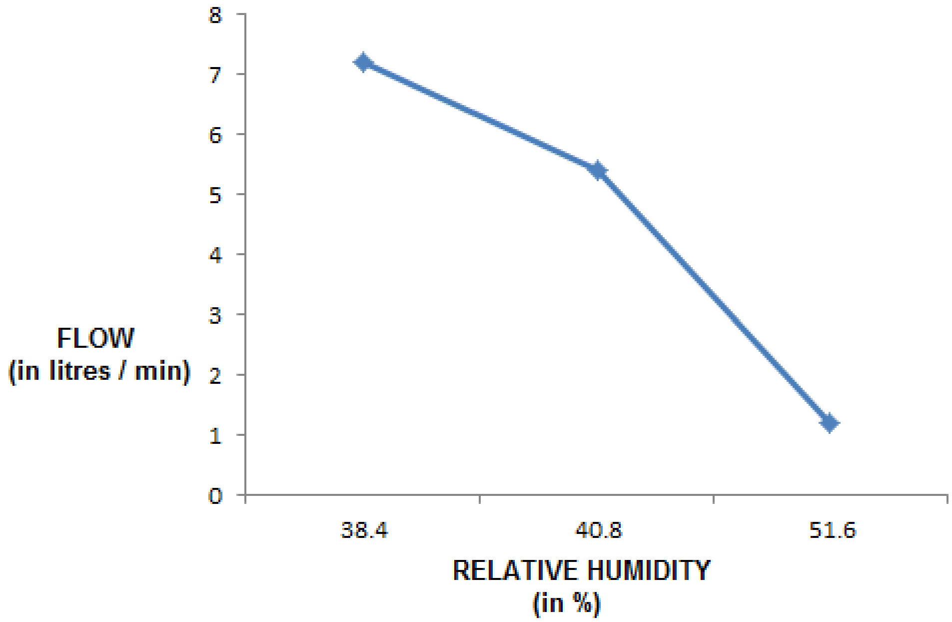


Fig. 4.13 Flow rate versus Relative Humidity at 10mm depth H_2O immersion

Both experiments showed a change of Relative Humidity of about 14% but the lower immersed sample at the 135 mm depth was able to produce a higher Relative Humidity in comparison to the surrounding atmospheric humidity, 11% higher than the 10 mm depth produced, at the same temperature and area of exposure. This suggested that the pressure does shift the potential to humidify the air, while the rate of humidification at a given pressure is dependent on temperature, area of exposure and the rate of flow occurring. Increased pressure will increase the capacity to humidify the air. This information was critical to achieve results in one of the final experiments of the study.

4.6.3 RESULTS OF TUBE SHAPED PT-NAFION CHAMBER HUMIDIFICAITON

In practice the hydrating and dehydrating of the Nafion by immersion in and removal from DI water and the material overlap with elastomer adhesive construction to form the tube caused a buckling and wrinkling phenomenon to take place that induced semi-permanent distortions in the Pt-Nafion tube wall geometry. These uneven undulations in the tube wall had two undesired effects: The CSA was distorted and so all the smooth wall flow assumptions would have been unreasonable, but also the unevenness of the overlap lines caused the material wall of the tube to split which prematurely ended these experiments.

The Nafion material, coated or uncoated, changed volume and length every time it was hydrated and dehydrated, so that it was not possible to construct a vessel where the pieces of Nafion had to be attached to each other and remain firmly bonded. The results shown in Table 4.3 clearly demonstrate the significant volumetric change that occurred when hydration took place. The surface transformation between the hydrated and dehydrated state caused significant distortions in the sheet flatness in all the experiments where the edges of the material were bound or bonded to another surface.

The minor change in temperature and humidity between the three flow rates and the differential between the water bath temperature and the air output temperature suggested that the air flow rate was too high to allow significant transfer of humidity to take place. The slower flow rate allowed a longer contact time of the air with the humidification window of the Pt-Nafion tube, so the resulting higher Relative Humidity value correlated with the conclusion that Pt-Nafion does allow water vapour to humidify air in proportion to the amount of contact the material has with the air. The longest contact time achieved by the slowest flow rate produced the highest Relative Humidity value and the shortest contact time of the highest flow rate produced the lowest Relative Humidity value.

Table 4.11 Humidity transfer results

Bath T in °C	Q sys in l/min	T air out in °C	RH air out in %
32	0.68-0.73	19.1	20.1
	1.03-1.07	19	18.7
	2.26-2.31	19.4	18.3
39	1.03-1.07	23.3	17.3
	2.26-2.31	24.2	17.3
47	2.26-2.31	32.2	17

The conclusion of this first set of experiments is that the "as prepared" Nafion Pt material could allow water to transfer across itself over the Pt-Nafion-Pt interface and produce humidification of the air coming into contact with the tube inner surface. The first condition was confirmed as possible by this experiment as seen by the results in Table 4.11.

4.7 PERSISTENT HYDRATION RESULTS

In the first experiment the water did not keep the beam portion of the material hydrated or functional. However, the idea of hydrating the IPMC in one location where there is no surface coating by putting the water into intimate contact with the surface and then the water migrating to the coated region, where it is needed for actuation, was one that did not appear to be reported in the literature. This study concluded that investigating the issue of persistent hydration was critical to resolving the question of whether having a one material solution to the pumping and humidification was feasible or not.

In the second experiment, the 43 mm height of the water column container was briefly able to hydrate the strip, and the previously non-hydrated material was able to actuate for just over 11 minutes before it ceased to move.

Table 4.12 Results for three different height based pressures to test transverse hydration

Height of water	Exposure Time	Result
1mm	1 hour	no motion from electrical stimulation
43mm	15 minutes	11 minutes motion from electrical stimulation
305mm	15 minutes	24 hours motion from electrical stimulation

In the third experiment the additional pressure from the increased height was able to transversely hydrate the Pt-Nafion and maintain motion for a 24 hour period while being electrically stimulated. The results of these three experiments were summarised in Table 4.12. This time value was significantly longer than any previous measured time value in the research period. (The time period observed was over 80 times longer than the longest previous value of 18 minutes).

Table 4.13 Volume of water passed through system into surrounding air in 24 hours

Height of water Start	Height of water end	Volume change	Duration
305mm	302mm	$39.6mm^3$	24 hours motion from electrical stimulation

The principal of transverse hydration, that water could be introduced into a non-moving non-coated area of a material and then it would move from the introduction surface and internally transfer hydrating water flow to a different area was confirmed by the experiment. The other outcome that was indicated by the results was that a volume of water had passed through the actuating membrane and moved into the surrounding air. This volume change was summarised in Table 4.13.

Based on the earlier hydration mass values obtained experimentally, the 400 mm^2 electrode would have been expected to take in 7 or 8 milligrams to hydrate. The water mass absorbed was a little over 39 milligrams, so the extra water would have been pushed along the entire hydration pathway and out into the atmospheric air.

This was the last set of results obtained to address the feasibility question for the study. In the final section, Chapter 5, the implications of this data were discussed.

The research undertaken in this study involved addressing many aspects of material processing and behaviour that have been addressed by other research groups in the past [17] . The facilities available to characterize the material properties and standardise the processes and outcomes range in size and scope significantly around the world. A university or lab that specialised in energy systems study, where hundreds or thousands of fuel cell experiments were conducted, would have a natural advantage, for this study, that was not present in this case.

In the following discussion, many of the items that were confirmed as possible produced outcomes that were not superior, in terms of performance, energy use or cost. In order for the proposed single material solution to be truly competitive as a solution, a large amount of optimization work would need to be undertaken to improve the performance from “possible outcome” to “preferred outcome”, and thus justify selecting IPMC selection over other methods of humidification and pumping. Controlling the conditions and measuring the results of many of these experiments, to the degree of accuracy that would be needed to optimise the results, was beyond the scope and resources of this study. However the areas where further study would add detail to the results were noted below.

4.8 COATING PROCESS

The platinum coating thickness was an estimate based on a number of assumptions. Even distribution of metal regardless of orientation in the depositing solution, no interference mechanically or chemically with the masking material processes, even interaction effect of the sanding process with the deposition process, uniform deposition effects for the one month shelf life of the chemistry and the use rate of six depositions not exhausting the deposition ability of the solutions. Any of these assumptions could lead to inaccurate data, if the exact deposition thickness of 1.5 microns of platinum per side were critical to feasibility.

Subsequent S.E.M. imaging work at A.U.T. Engineering department confirmed that the coating was just around 2 nm thick, giving the ratio of the total thickness to coating of about 45:1. This ratio can be held as a bench mark value, but is not far away from the 30:1 ratio that other typical coating processes reported in other studies. If the coating technique could not be increased in thickness, a thinner Nafion material could be sourced, if a specific coating to thickness ratio was determined to be important to optimizing the mechanisms investigated.

Thickness of Nafion substrate, alternate ionic polymer substrates, thickness of coating, uniformity of coating or the purposeful forming of a gradient coating, the variation of metal alloys instead of a single metal deposit or a metal / non-metal hybrid deposit, identifying and investigating the direction of production of the Nafion substrate used were all variables that could be considered and quantified to confirm that the coating, humidification and actuation properties of the IPMC produced could be altered and possibly improved. All of these variables might improve or hinder the performance of a particular mechanism. For example, a thicker metal coating could allow more energy to be applied to actuate the IPMC, but the work-hardening of the extra thickness may reduce the longevity of the material and inhibit humidification channels or decrease deflection. These counter balancing aspects of every experiment and design choice would require future work to identify what the optimum ratio of deposition thickness to actuation and humidification values should be for a given application. Ultimately, all the device requirements for a specific application would be needed to determine if the experimental results were able to produce a real alternative for practical use.

4.9 PERFORMANCE CONDITIONS

Many of the original operating conditions where Ionic Polymer materials have been used, developed and improved were very different than the conditions that are permissible in the application space for this study. High temperature and high pressure conditions, with operating chemicals that would be toxic to human tissue were just some of the differences between the fuel cell and human tissue operating spaces. In addition, the primary interface relationships of fuel cells involved liquid-membrane-liquid contact, instead of gas-membrane-liquid contact. These differences make this study's investigation one where the possibilities of the materials have to be investigated carefully, in order to take the promising and relevant properties of Ionic Polymers and search for methods to overcome the additional constraints of the medical device application space.

Real design ranges for flow rate of the respired air, temperature ranges of operation, humidification minimums and maximums and energy amounts and costs, package space preferences and typical design life and disposable costs all have to be specified and verified in order to confirm the viability of the findings to produce a commercial conclusion.

For the study work, 6 litres per minute was the assumed minimum target flow rate for the air and humidification to achieve a minimum rate of 50% relative humidity.

The study confirmed that platinum coated Nafion can actuate when stimulated by a DC or AC electrical signal. The force produced, for the given material properties available from the fabrication techniques selected, were quantified. The electrode fabrication technique and the distribution of the metal and composition of the metal were not optimised. The speed, power, durability and repeatability of the motion were not optimised for the motion of the IPMC beam. If the air flow capacity and geometry of the air delivery vessels was specified or optimised for a preferred volume of delivery, it would be possible to utilise many of the reviewed techniques to investigate the best properties for the above actuation criteria.

Electroless polishing, gradient deposition, active deposition coating and multi-shape mask preforms all allow significant degrees of control and design to be implemented in the fabrication of actuators. None of these techniques could be employed in this first study of feasibility. All of these areas would be good candidates for further study of the actuation mechanisms.

The actuators for this study were manufactured using the most accessible deposition technique and were only controlled for thickness by repetition of technique. Investigating the shape, accurate thickness control, constituent metal alternates or blends and shape of deposit profiles would all be variables that could improve actuation properties in future studies.

4.10 ACTUATION

The actuation verification took several stages to be accomplished. The first important confirmation was that it was possible to actuate. But rapidly after mere actuation was confirmed, the result led to investigating what conditions were necessary for actuation and how can the actuations achievable be utilised? Answering all these questions in one feasibility study involved considering the effects of hydration, or more precisely what would occur in the absence of hydration and what mechanism could accomplish persistent hydration. The mechanisms for pursuing actuation were briefly considered, but the purpose of the geometries considered was to give a framework for a possible calculation of numbers of actuators and approximate sizes of components. This portion of the study took certain physical aspects of the actuation and incorporated them into holding and channel configurations that mimicked and adopted the primary features of the experimental fixtures as a product. This method simply allowed typical assumptions to be utilised to consider a possible application device. The actuation pathway from the high speed video was used to determine an actuation profile. This shape was used in conjunction with **The Handbook of Fluid**

Dynamics to design an enclosure chamber for the actuator. The edges of the CAD model were used to fabricate translucent chambers to test the planned flow and help visualize the flow pattern. The extremes of the assumed positions of the actuator were modeled as solids at the extreme toggle positions of the Pt-Nafion material relative to the enclosure walls. Empty chamber flow versus Pt-Nafion in place flow was modeled to attempt to determine the effect of oscillation in the chamber.

The flow of the air through a theoretical enclosure was modeled based on the recorded oscillation geometries and from the 10mm strip deflection video. The 10 mm x 37 mm beam size was selected for maximum force from the force experiments and the cantilevered beam as an actuator was selected due to the relative superiority of the results against the diaphragm design results. A diffuser after the chamber was considered, but at the flow rates that were observed experimentally, no geometry that was modeled produced clear results.

This spiral stack theoretical design could be used to place eight 10mm wide IPMC beams in a spiral arrangement so that the cumulative flow pattern would add into the centre of the flow channel chamber to generate a net flow of 8 times the single beam flow value in theory. A theoretical arrangement of this concept was represented in a CAD design drawing shown in Figure 4.14. Taking the lowest measured air flow value of 0.02 litres per minute, obtained from experimentation, this would imply a total of 0.16 litres per minute per layer in 12 mm of stack height.

In order to achieve 6 litres per minute of air flow, if each actuator remained perfectly efficient at that flow rate, would take 38 layers or 456 mm of stacked layer elements.

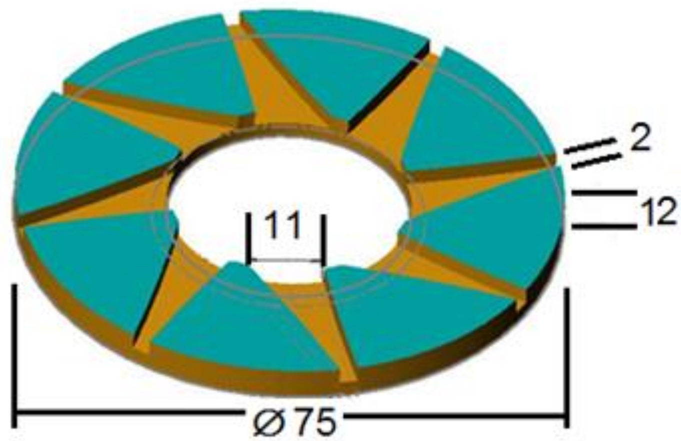


Fig. 4.14 Theoretical eight chamber inward flowing spiral stack design

The experimental set-up of the enclosure experiments had the actuator oscillating side to side, whereas many of the other actuation experiments had the beams oscillating up and down. Inducing a spiral air flow pattern could avoid the flow progressing straight into the far side of the centre flow channel (arriving perpendicularly to the surface of this channel). Entering the channel at any angle less than 90 degrees should help to induce flow, rather than inhibit it.

The orientation of the actuators and all the practical interface issues such as hydration, electrode contact, actual angles of position, flow direction relative to actuation position, flow channel geometry, coordination of actuator motion and all the other details of producing real flow would need to be the subject of further study. The proportions and the size and area of a device based on these numbers would be believable as a method. A device with 300 to 600 actuators is conceivable for a flow device.

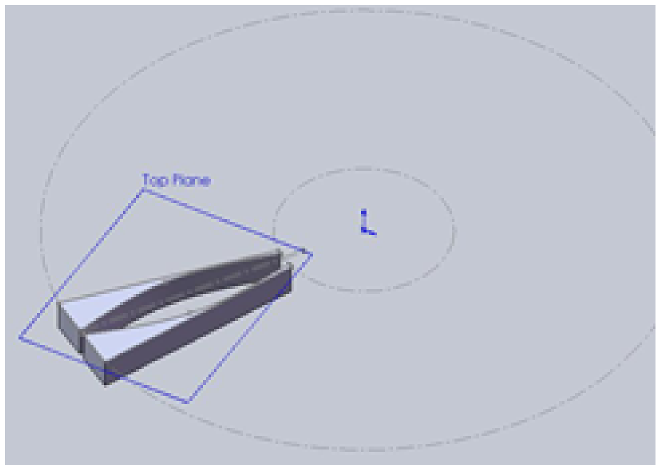


Fig. 4.15 An enclosure shape that decreases the output area, but mimics the oscillation shape might increase flow speed

The study scope did not include optimizing the enclosure's actual shape, but experimental chamber designs did produce a measurable flow that could be multiplied to produce the flow volume required. One area of possible improvement was chamber profile and a variant that was drawn but not constructed is shown in Figure 4.15. The starting portion of the chamber needs to mimic the shape of oscillation, based on the three shapes tested, but this study did not determine the best post actuator profile for flow.

4.11 HUMIDIFICATION

The study confirmed that the as-built platinum-Nafion material would allow humidification of air to be delivered from a source of water to air and that an increase in temperature improved this delivery in the range of temperature that an human delivery device would operate in (20°C to 40°C). The literature suggested that the platinum coated Nafion would allow such humidification, as was demonstrated in the initial experiments, to occur. The other aspect of the Nafion interaction with water was hydration.

Hydration and humidification are interlinked with each other in all of this work. The relationships between hydration, humidification, actuation and design requirements need to be investigated further to produce minimum interaction values for the parameters needed to achieve a particular outcome. For example, one experiment showed “natural hydration” by immersion in DI water of coated and uncoated Nafion occurred with no additional stimulation required with a range of uptake between 3% and 19%, by mass, of water into the IPMC or Ionic Polymer alone. These hydrations always took place at room temperature and the dehydration process of removing the source and actuating, or not re-applying the source would lead to de-hydration. Feasibility was the primary goal in these investigations and hydration could be achieved by immersing the IPMC material in water for ten minutes, so hydration was achieved. Optimising the hydration by relating the process to temperature, coating types, thickness of coating and investigating the microstructure of the materials and determining what factors drive the process are all areas where improvements could probably be made. These factors were noted as variables for future work, but not included in this study, since the goal for this study was combining two functions, not improving one function.

Humidification of air utilises hydrated material, since the material becomes hydrated to transport water across or through it to place the water in the air. Actuation requires hydration since the gel behaviour that the electrical stimulation produces has to have hydrated polymer to occur. Both of these processes are critically linked to hydration. The difference is that humidification can take place in a material that is not moving and actuation, by definition, cannot.

The biggest obstacle to overcome for this study was how to hydrate, and keep hydrated, Ionic polymer material while actuation occurred. What the experimental evidence pointed towards was that for hydration to remain, persistently, a source of hydration had to remain connected to the material and a method of transporting that hydration water source throughout the material had to be adopted for hydration to remain functional for the continued actuation mechanism of the material to function.

The hydration and actuation investigations of this study have identified that pressure of water through hydrostatic head can drive water to enter the surface of the Nafion material while it is in intimate contact with the material and then the same method forces the water through the rest of the material and into the actuating region of the material. The term “transverse hydration” has been applied to this technique and allows the hydration source to be connected to the material in the non-actuating region where platinum coating has been held back, and then the coated region that is actuating receives water internally and maintains the hydration quantity at a sufficient level to allow the actuation to persist. In addition to hydrating the whole material, the transverse hydrating mechanism allows the material to pass further water into the air surrounding the actuating portion of the oscillating beam. This hydrating function is only occurring in addition to the hydration need that was identified. The first successful sustained transverse hydration experiment had the additional bonus of producing 39.3 mm^3 water introduced to the surrounding air. This discovery warrants considerable further investigation.

If the actuation design above were to incorporate the same amount of moisture introduction from actuators as the number needed for actuation, (306), then that would be just under 12,000 mm^3 of water in 24 hours. 6 litres per minute is 8.64 m^3 per day. With this volume, defining the number of actuators needed to condition the air will require setting the temperature, pressure and percentage of relative humidity needed as firm design goals. Obviously, the temperature of the system as well as the flow rate and contact areas of the mechanisms will all affect the final efficiency of the system.

Investigating all of the details of the transport mechanisms that were indicated by the experiments conducted will allow the transfer rates and mechanisms to be further understood and improved upon in future experiments. An example of the experiments being improved on would be modifying the small square hydration chamber with vertical slit attachment to allow the tall 305 mm column to be connected into the top and then the Nafion strip can be fed into the vertical slit chamber instead of connecting the pipette to the top side of the strip only. This arrangement would allow side to side motion of the actuator, as had been determined to be more symmetrical for the oscillation motion, and increase the area of contact to the water by more than two times the area of the pipette end alone. In the theoretical ring stack design, the edges of the chamber at the outer diameter of the ring could be modified to contain hydration cells where pressurised water could flow down from a gravity fed source, or could be pressurized by a secondary power source. By altering the shape of the actuators, the air flow could be optimised to have a slight downward flow profile to take advantage of gravity to improve the flow and increase the efficiency of the system.

In the course of running these experiments, it was reinforced that the issue of the material hydration was critical to all actuation and humidification mechanisms.

4.12 CONTROL IMPROVEMENTS

4.12.1 ALTERNATIVES TO NAFION, PLATINUM & STANDARD FABRICATION METHODS

Once IPMC's had been identified and selected as the area of material to study, the variables that were considered for fabrication of the actuators were the alternatives to review. What polymer substrate [14] and what metal or coating material [12] would be best to use in the study and what factors of variation would provide suitable control were the key issues to address? The morphology of the electrodes [54]of the polymer electrolyte actuator was a consideration for the designs especially as it related to the actuation of the IPMC specifically fabricated [26].

The specific choice of metal for the electrode will have effects on the durability, decay rate, corrosion resistance and all the other physical aspects of the surface interaction with the polymer and the environment. One alternative to platinum was silver[11].

Another aspect of the true refinement of the material set up was minor component enhancements. The addition of relatively small amounts of a trace element, in this case iron Fe at a little over 3.10% at different depths has easily measurable effects on improving and increasing the modulus of the base polymer, in this case Nafion [98].

Once a market is established, as was the case with fuel cells, there is no question that multiple manufacturers will produce equivalent or similar products. This was the case with poly(perfluorosulfonic) compounds [99]; where DuPont had Nafion, Dow produced Aciplex as a competing fuel-cell polymer membrane system. There are others as well [9], but the discussion point was the same for all of these materials. The backbone molecule is a polyperflourinated construct that will allow the chemistry of fuel cell activity to take place and then as a result of this atomic geometry, other coating based behaviour is possible, which is where the actuator work commenced for the consideration of this study.

With the multiple candidates to choose from, on a large scale project the choice would involve careful characterization techniques for the intended purpose [41, 100], but for this study and the resources available, it was decided to select the material with the most history, the most citations and the most established chemistry and material behaviour of all the Ionic Polymer materials: Nafion.

4.12.2 ELECTRICAL STIMULATION REFINEMENT

The width and length of the actuation beams was selected from a relatively small number of experiments and with very limited options for actuator design and materials fabrication techniques. All of the variables available for fabricating better refined electrodes could be investigated with the knowledge that methods to keep hydration consistently running could be employed to justify the investigation. The microstructure features that allow the transverse hydration travel and the humidification to take place can be selected as the focus of further investigation and isolated experiments, designed to improve the humidification amounts and rates of water flow and dispersion through the materials. The best width to length ratio could also be investigated.

The maximum deflection of oscillation was obtained for a particular geometry of electrode, but the shape was a simple and symmetrical shape. Sufficient study of options for that actuator design would determine if there was a better shape for efficiency and suitability to produce air flow at the speeds, volumes and temperatures needed for the application that this study intended. Once best shapes of electrode, substrate and masking pattern had all been investigated more thoroughly, then the optimum frequency and voltage for the electrical stimulation could be studied to improve this area of design as well. The humidification levels might be aided by strategic channels of non-coated areas or increased coating thickness in some areas and decreased thicknesses in others. Understanding the detailed behaviour of the material with regard to the movement of water based on the electrical stimulation will allow the interaction of electrode design issues, electrical stimulation and humidification to be optimised for this type of actuation-humidification work.

4.12.3 GRADIENT COATING

Depending on the geometry of the actuator or actuators for any final designs, it is very likely that the actuation motion will produce a pattern of un-even stress, or that there will be areas of greater and less stress over the face of the actuator or actuators. Different actuators in a series would be likely to show different stress patterns based on different flow and load experiences. Since this uneven stress distribution is extremely likely to be a one of the issues that will need a solution, one of the tools to address refining and unifying stress distribution is fabricating gradient electrode coatings[ ][96] . Varying thickness and depth of coating are two of the variables, or varying the thickness of the substrate itself are all ways that the overall thickness and ratio of electrode to substrate can be determined.

4.12.4 SHAPE OF ENCLOSURE

Aerodynamic and hydrodynamic simulation of the surrounding chamber shapes and the true flow of the air and moisture around the oscillating beam would allow the chamber to be optimised to improve gas flow from the actuation. Studying the motion of the actuator to investigate the limits of the actuation behaviour, in terms of motion decay or work hardening would be critical to determine if the long-term behaviour of all the observed mechanisms would stay within a usable range for a commercial application. The durability of the mechanisms observed in this study would need to be verified, with significant volumes of repetition over longer periods of time. The indications that improvements could be confirmed and improved upon are in evidence, but commercial viability would require more vigorous investigation, in order to commit further resources to research developing this type of device.

Actuation in a structure to produce air flow had been demonstrated to be possible with the as-built materials. As a final exploration of this enclosure chamber concept, several tentative multi-beam layouts were built as CAD designs, to suggest how a mechanism could be constructed to produce a usable air flow. None of these concept designs were fabricated as the study purpose was a feasibility of materials study and not a device fabrication investigation. The designs were intended to show that application constructions could be envisioned, based on the materials experiments evidence.

CHAPTER 5: FUTURE WORK AND CONCLUSION

5.1 SUMMARY OF EXPERIMENTAL ACHIEVEMENTS

The purpose of this study was always to determine if a single material could be used to pump air and humidify it at rates that would make it useful for conditioning air for human respiration in hospital and home medical applications.

The initial indications are that it would be possible to achieve this aim with commercially available Nafion and Platinum, based on the following experimental results:

1. The experiments conducted confirmed that the manufacturing method described in the literature worked and produced a material that actuated.
2. The stimulation of the material actuation could be varied by varying the electrical signal being applied to it, so control of the motion could be achieved by electrical signal and electrode design.
3. The motion could be used to move air along a closed path.

4. The material could deliver humidity to surrounding air.
5. Hydration of the material, a critical precursor factor for actuation and humidification functions, via transverse hydration, was able to be sustained for 24 hours.

This last achievement represented the critical obstacle to considering the material for a real application. Prior to the achievement of sustained hydration, the longest period that the actuating IPMC had been able to continue actuating was 18 minutes.

This time extension of the critical properties of the key mechanism for viability of the materials removes the most obvious barrier to producing a product. 18 minute functionality is not viable and 24 hours is. There are still all of the cost, functionality and robustness and performance issues that would have to be convincingly studied for repeatability and ranges in a truly commercial device, but the experimental evidence can be considered to show that is would be feasible that a device could be built to pump and humidify air for human respiration.

5.2 COMMERCIAL CONSIDERATIONS

Providing experimental evidence that a series of mechanisms are possible to produce a physical result does not mean that the results *should* be combined and utilised to do so in a commercial setting. The efficiency of the effects that were studied was not determined, so the actual running costs to produce and use the materials and mechanisms and the comparisons to the current costs of existing equipment would have to be investigated and carefully reviewed before further development was considered. Given that a single 150 mm x 150 mm sheet of Nafion was over USD $143 in 2009, and at least seven sheets would be needed to produce one unit if all the material efficiencies from the study assumptions were correct. This would lead to a Nafion only cost of USD $984. If the platinum, electrical controller, housing development and medical verification costs are added to the cost of developing an actual device around this technology, then some aspect of the mechanisms studied would have to be identified that produced a significant market advantage over other methods currently available. More accuracy of humidification control, more dynamic flow control of direction or flow rate or some other aspect of flow, package size of the unit in the operating space (smaller or more convenient), lower production costs, once commercialisation is achieved, greater longevity, more reliable or durable operation or some other significant advantage would have to exist to justify pursuing the implications of this study to achieve a commercial device.

5.3 FUTURE WORK

Many of the implications of the results will imply further work. The typical commerci al process of evolving device features and functions from lab results to optimised commercial mechanisms would be an obvious area to focus on for next steps from this study:

- Reviewing all the materials that can be used to build IPMC's today
- Generate a cost per area value of the materials available for comparisons
- Estimate commercial unit costs based on optimised material selection.
- Confirm the hydration, actuation and force performance of the least cost IPMC
- Determine if the cost of producing a unit could be considered commercially.
- Computer optimise pump and humidity functions to confirm deliverable need
- Confirm Nafion and Platinum superiority against all other candidate materials
- Identify significant functional advantages before pursuing commercialisation

5.4 CONCLUSION

In conclusion, the evidence of the experiments from this study showed that pumping and humidification can physically be achieved with an IPMC material such as platinum coated Nafion. The achieved rates of flow and humidification for use in human respiration devices would both need improvement to be considered for commercial development.

The efficiency and cost of the mechanisms that were investigated were not considered for this feasibility investigation. Adding these considerations to the criteria might change the utility of these materials as an option for simultaneous actuation and humidification.

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