Department of Precision and Microsystems Engineering

Conducting Polymer Microfluidic Valve

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Challenge the future

MSc thesis
Conducting polymer microfluidic valve

by

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SUMMARY

Conducting polymers are a class of polymer materials that can conduct electricity, unlike the conventional polymers like rubber and plastics. The traditional properties of polymers still remain, this includes strength, stability, flexibility and flexible fabrication and handling methods. The electrochemical expansion of conducting polymers has been widely used in numerous studies, ranging from self-positioning micro electromechanical systems (MEMS) to bending beam artificial muscles. These applications of electrochemically expanding conducting polymers include numerous studies with soft actuator that replace traditional actuators like motors with contracting strips of conducting polymers, called artificial muscles. The application of conducting polymers as microfluidic valves have been studied less frequently and have a wide range of challenges to be solved in order to be used outside of scientific studies. Important advantages of conducting polymers are the low actuation voltage of less than 1 volt and the flexibility of the material. Another advantage is the relatively easy and customizable fabrication techniques: The conducting polymer electrode layer can be deposited using techniques like spin coating, sputter coating, inktjet- or screen- printing or even patterning using hot or soft embossing. The electrochemical polymerization of a layer of active expanding conducting polymer is highly customizable and various fabrication techniques are often possible without using a cleanroom.

The main research question is: *Is it possible to design and fabricate an all polymer modular low voltage microfluidic valve with conducting polymer that has a switching speed of less than 500 ms?* During this project several methods were created and explored to make the basis for a fully polymer micro actuator with the ultimate application in a microfluidic valve system such as a lab on a chip (LOC) device. This actuator consist of three layers. The first layer is the flexible base layer that also functions as a fluid barrier in the microfluidic system. The second layer is the electrode material that is used for both the deposition surface during the polymerization of the expanding conducting polymer and as the main electrical conductor during actuation. The final layer is the electropolymerized layer of expanding conducting polymer. Polydimethylsiloxane (PDMS) and cyclic olefin co-polymer (TOPAS) were investigated for the flexible first base layer and poly(3,4-ethylenedioxythiophene) (PEDOT) and gold were both used as the electrode material. Various solutions of pyrrole and dopants were used to make the active polypyrrole (PPy) layer using electrochemical polymerization. These different Dopant and electrochemical systems characterised in terms of polymerization speed and morphology differences.During the project a great deal of effort was put into interfaces adhesion of TOPAS-PEDOT and PEDOT-PPy. Furthermore the limited conductivity of PEDOT was studied with respect to the electrochemical polymerization and actuation characteristics of polypyrrole. This study into the fabrication of an all polymer 3 layer beam actuator (to be used as the basis of a microfluidic valve) led to a number of protocols. These protocols describe the pre-treatments, pre-mixing, spin coating, drying, handling of samples, and test/fabrication setups. In order to investigate the new method of using PEDOT, actuator systems with PEDOT electrodes were compared to systems using sputter coated gold electrodes. The new materials and fabrication methods are used to form an outlook about the possibilities of using the investigated methods in microfluidic systems, with particular applications such as disposable microfluidic systems that can be commercially used.

PREFACE

The main focus of this MSc thesis report is gaining insight into the design of an conducting polymer microfluidic valve. The main research question is:

Is it possible to design and fabricate an all polymer modular low voltage microfluidic valve with conducting polymer that has a switching speed of less than 500 ms?. The research question will be answered in the following four chapters : The introduction to the state of the art, the experimental approach and methodology, the reflection and the appendices.

The introduction will cover the state of the art of different studies which are relevant to consider to be able to understand and to improve conducting polymer microfluidic valves (CPMV). Furthermore the motivation, challenges and goals of designing a conducting polymer microfluidic valve will be discussed. The main research topics on conducting polymer microfluidic valves will be addressed in a particular sequence in order to introduce all the basic concepts. In order to understand the principles of the expansion of conducting polymer materials; polymers, conducting polymers and the expansion process will be discussed in detail. Subsequently the basics of conducting polymer actuators will be addressed by explaining the fabrication, actuation and applications. The final part of this section will introduce the application of conducting polymers in a micro fluidic valve. This section will focus on microfluidics, lab on chip devices and the final applications in which the plans for a new type of conducting polymer microfluidic valve will be introduced .

The second chapter will focus on the different aspects of the conceptualisation and creation of a conducting polymer microfluidic valve. It starts with the introduction of the methods and materials used for the investigation in choosing the right base, electrode and active material layer. This is followed by describing experiments in which particulars of these different possibilities are checked for their feasibility in an actuator. Subsequently the results of this project will be discussed and based on these results a conclusion is drawn. Suggestions and opportunities for further research regarding this technology will be presented in the outlook section of this chapter.

The third chapter of the report will elaborate on the reflection regarding the entire project. In this chapter the initial timeline is compared to the actual timeline, and pre-determined pivot points are discussed. The line of though will also be presented which will show the decisions that were made. This will be followed by contributions delivered by and received from people around the MNE and/or PME groups. Finally a reflection of the used literature is made, important individual papers are discussed and groups that work with conducting polymer actuators are mentioned.

The fourth and final chapter will display the appendices and will encompass most of the specific experimental details and protocols.

Sam Smit
Delft, June 2017

CONTENTS

1

STATE OF THE ART

1.1. MATERIAL: EXPANDING CONDUCTING POLYMER

1.1.1. INTRODUCTION

This State of the art chapter is an introduction to different studies which are important to address in order to understand and to improve conducting polymer microfluidic valves (CPMV). Furthermore the motivation, challenges and goals of designing a conducting polymer microfluidic valve will be discussed. The main research topics on conducting polymer microfluidic valves will be addressed in a specific order to introduce all basic concepts. The state of the art scientific knowledge about expansion of conducting polymer materials polymers will be introduced with a study from Berdichevsky [1]. This study will introduce most of the concepts regarding expanding conducting polymer microfluidic valves. The polymer material which is the base of the design will be discussed first. This will include a base understanding of Polymers, a particular group of polymers called conjugated polymers (conducting polymers) and the reduction oxidation (redox) reaction that stands at the base of the expansion properties. Finally some applications and opportunities of the material will be discussed. Thereafter the basics of conducting polymer actuators will be discussed by explaining the fabrication followed by the actuation and applications. Lastly the application in a micro fluidic valve will be divided in microfluidics and lab on chip devices. This is followed by the applications in which the plans for a new type of conducting polymer microfluidic valves will be introduced.

1.1.2. POLYMER

Conducting Polymers can best be classified as being part of the main group of Polymers. Polymers are materials in which many units form a large Molecule and can be synthetic like most plastics or made in nature like latex rubber, DNA and proteins. Most of the synthetic polymers have a linked carbon (organic) backbone and consist of a monomer (like pyrrole, figure 1.6a) that is polymerized into a larger chain of recurring units, called polymer (like polypyrrole, figure 1.6b).
This monomer is one of the factors that determines the properties of the polymer material. Some monomers like pyrrole will become electrical conducting polymers (more in section 1.1.3). Other polymers such as Cyclic olefin co polymers (TOPAS ®) may consist of a mixture of Ethylene and norbornene. This TOPAS has the following properties of being transparent, strong and chemically resistant. When the mixture rates of Ethylene and norbornene are changed, the properties like glass transition temperature can be designed to be between 70 and 180 degrees Celsius.
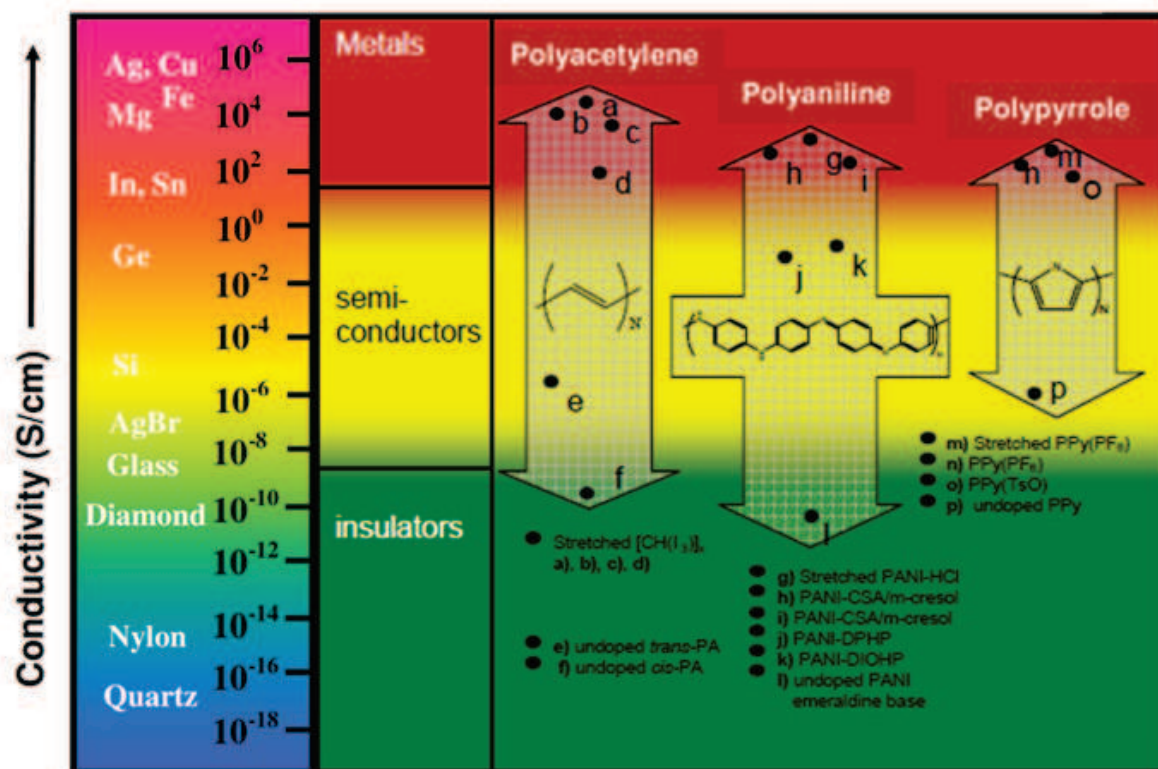
1.1.3. CONDUCTING POLYMER

Figure 1.1: Conductivity comparison of different conducting polymers versus various other materials , Parveen Saini 2012.

Conducting polymers are special types of polymer that, in contrast to most polymers, can conduct electricity in such a way that it comes close to the conductivity of some metals (see figure 1.1). A lot of research is available on the conducting polymer poly(3,4-ethylenedioxythiophene) also called PEDOT [2]. Conductive polymers were discovered in 1977 by Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa [3]. In 2000 they received the Nobel Prize in Chemistry for the discovery and development of conductive polymers [4]. The special properties of Intrinsically conductive polymers (ICP) are described by the University of Liverpool as:

'Delocalized electrons along the conjugated backbone of polypyrrole result in an extended pi-system which is filled with valence electrons. Adding or removing electrons from the pi-system (doping) produces a charged unit called a bipolaron unit which is capable of conducting electricity.'

Conjugation is the overlap of the p orbital (electron), this is what allows the decentralised electron to belong to a group of atoms. This is possible because of the backbone of the material that alternates between single and double bonds(pi-system). The result is that electrons can transfer a current over the material. The (most electrically) conductive variant of polypyrrole is in the oxidised state (see figure 1.4a).

POLYMERIZATION
Conducting Polymers are made by an (electro)chemical reaction in which the monomers come together in chains. The nucleation point of these chains can be on electrodes to coat an already conducting surface with a conducting polymer. Most of the applications in expanding conducting polymer use electropolymerization because of the numerous advantages. The most remarkable advantages of polymerization are the controllability of the chemical process and the adhesion of the polymer to the electrode.

Pyrrole is the most commonly used monomer to make the polypyrrole conducting polymer actuators. The polymerization reaction of polypyrrole can start by applying a low voltage below 1V (versus a Ag/AgCl reference electrode) on a submerged system of electrodes, see figure 1.2. This system consists of a working
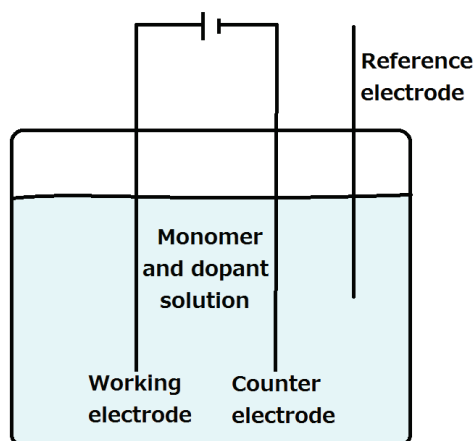
Figure 1.2: schematic view of electrochemical polymerization setup inside a glass beaker.

electrode where the polymerization will take place. The counter electrode will supply the electrons that are needed for oxidation reactions, the silver reference electrode will measure the voltage.

During this reaction the pyrrole is transformed into polypyrrole, see figure 1.3. The first step (A) is the oxidation of the pyrrole monomer to form a free radical cation, this means the molecule has a unpaired valence electron. The power for the oxidation of the monomer is supplied by the electrical potential on the system. Following is the formation of a pyrrole dimer when 2 of the highly reactive free radicals bond together (Step B). Step C shows the elimination of hydrogen, followed by the further oxidation (Step D) to form a chain.
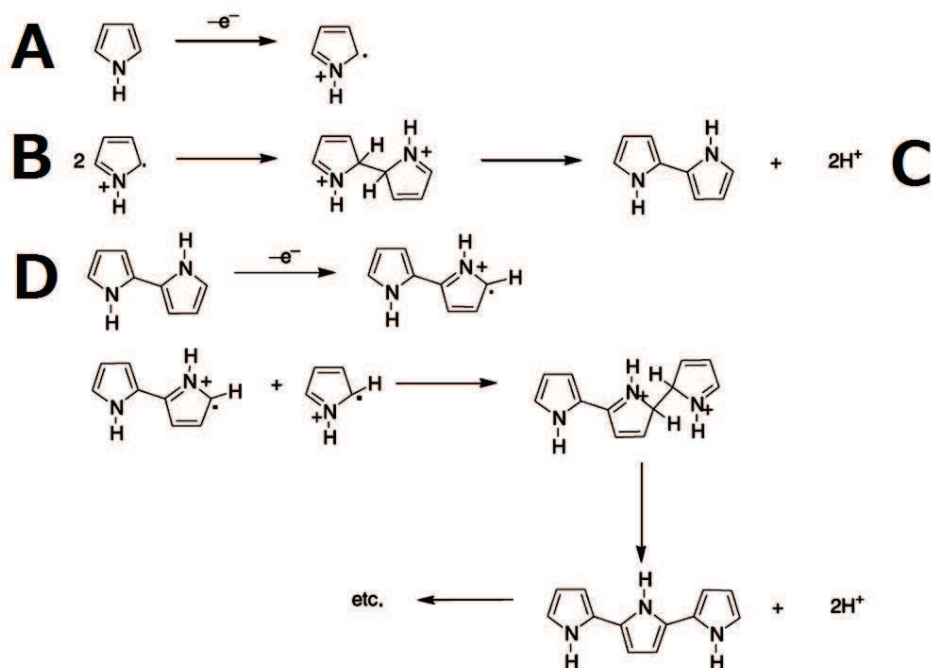

Figure 1.3: Polymerization of polypyrrole[5], important steps indicated by A to D.

A higher voltage will increase the polymerization speed, but over oxidation of the polypyrrole will occur at the oxidation potential of water [6], this is around 1V (vs Ag/AgCl). This over oxidation will render the polypyrrole layer insulating and inactive. Another variable in the electrochemical process is the concentration of monomer and dopant. The dopant will be entangled into the matrix of the polymer material, this will be used to make design an optimal expansion of polypyrrole, see section

(b) Molecular structure of NaDBS, Sigma Aldrich
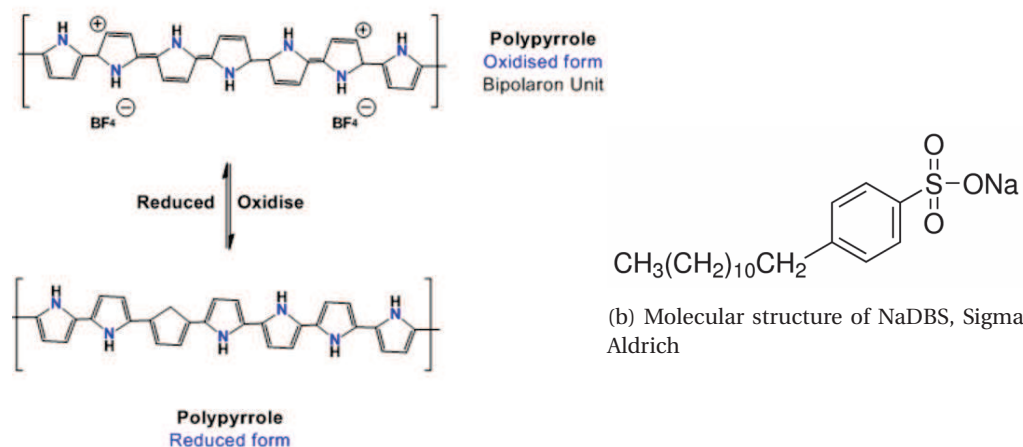
(a) Conducting Polypyrrole (PPY), University of Liverpool.

Figure 1.4: Chemical structures of oxidised and reduced polypyrrole, accompanied by the structure of Sodium dodecylbenzenesulfonate.

1.1.4. EXPANSION PROCESS

The expansion reaction takes place when an electrical potential is applied over the polymer material, when the material is submerged in a electrolyte solution that contains small ions. This solution contains charged particles (ions) and the chosen cations or anion can be different from the initial deposition dopant solution. The potential will set a redox reaction in motion in which ions move in or out of the matrix of the polymer material. This displacement of ions will cause the material to expand and contract. This expansion is mainly because of the changes in the polymer backbone when ions must be incorporated into the matrix of the material. A second expansion effect is the osmotic expansion [7]. This expansion is indirectly caused by the insertion of ions into the polymer material because this will make the solvent molecules move into the polymer material. This osmotic effect can change when the dopant concentration is optimal. [8] Furthermore the stiffness of the material will also change during the redox reaction, during the contraction of the material in a 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF6) solution the Young's modulus can increase up to 200 percent [9].

There are multiple polymer materials that can be used as an actuator, but polypyrrole [10] [1] is most commonly used in previous studies. This is mostly because of its good expansion rates and reliable functioning. Polypyrrole is commonly used in combination with Sodium dodecylbenzenesulfonate (NaDBS, see figure 1.4b) as a dopant [11]. This salt will dissolve in a solution before the polymerization of the polypyrrole and will be entangled in the structure of the polypyrrole because of its long molecular structure. This incorporation of the DBS molecule will give the PPY a charge that can be used to attract ions out of a solution into the matrix of the PPY structure when a potential is applied. This incorporation of ions will cause swelling in the two ways which were discussed before. The reaction (figure 1.2) shows that Na+ from the NaDBS is separated from the salt, an electron will be supplied and the Na+ ion will move into the material will move into the matrix of the material.

$$PPy^+(DBS^-) + Na^+ + e^- \longleftrightarrow PPy^0(NaDBS) \tag{1.1}$$
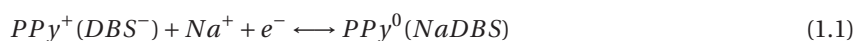
1.1.5. EXPANDING CONDUCTING POLYMER

In the research by S. Wilson et al.(2007)[12] an interesting summary is given regarding what kind of applications have been developed with conducting polymers:

some interesting applications of these materials have been developed, such as light emitting diodes, solar cells, transistors, diodes, holographic storage media, chemical and biological sensors, capacitors, batteries, anti-static coatings, electromagnetic shielding, anti-corrosive coatings, gas and liquid separation membranes, artificial muscles, lithography and metallization, photo-electrochromic devices, xerographic photoreceptors and all-polymer electronic circuits. Several companies involved in commercialisation of conjugated polymer devices include, Pioneer, Dupont, Cambridge Display, Infineon, Kodak, Sanyo, Philips and TDK.'.

The expansion of conducting polymer can also be exploited for the creation of 'artificial muscles' when the contraction of the material is used to bend an actuator. (see section 1.2.1). Although electrochemically polymerized conducting polymers can be described as artificial muscles, there are other kinds of polymer actuators techniques like electrostatic, pneumatic, piezoelectric, thermal and ionic polymer-metal composites that all have specific advantages. Some of the main advantages of electrochemically polymerized conducting polymer artificial muscles over other types of artificial muscles are the low actuation voltages of less than 1 volt, the continuous power, efficient positioning over time and the relatively easy and customizable fabrication methods.

INTRODUCTION INTO THE INTERDISCIPLINARY FIELD OF MICROFLUIDIC VALVES

A good example of the application of conducting polymer as a microfluidic valve is researched by Berdichevsky [1]. This study shows a thick polypyrrole actuator layer on top of a protruded post made of gold on a silicon wafer. This expanding layer is used to close a flexible PDMS microfluidic channel, see figure 1.5a. The entire system is made by using micro fabrication, see figure 1.5b, the polymer (section 1.1.2) is electrochemically deposited (section 1.1.3) using a solution of pyrrole monomer and NaDBS dopant. This dopant will allow the material to have a special redox reaction in which the material expands (further explanation can be found in section 1.1.4). Equation 1.2, shows the reaction in which ions will move into the matrix of the material and cause the material to swell. This reaction requires a low voltage of less than 1 V. The actuation in this particular study uses the an isotropic volume change in the direction normal to the surface of up to 30 percent, see figure 1.5b, corresponding to an initial displacement of $11\mu m$.
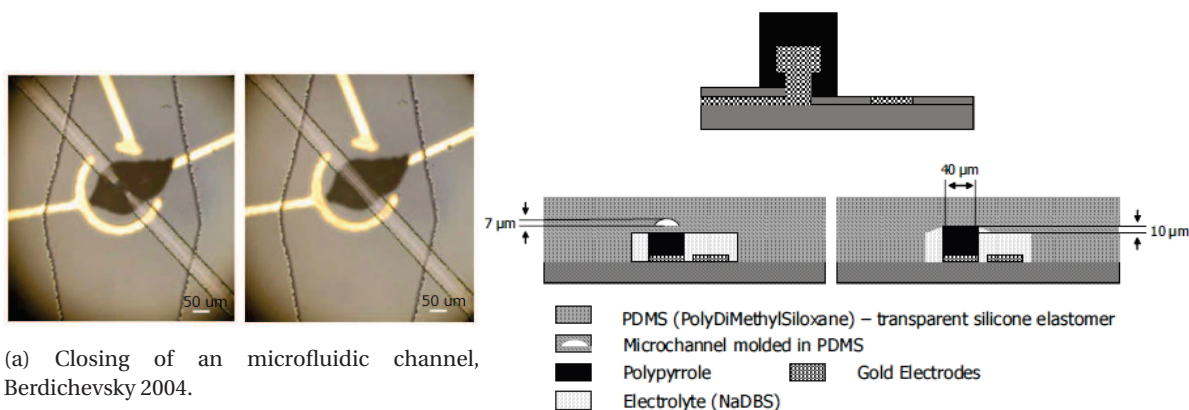
(a) Closing of an microfluidic channel, Berdichevsky 2004.

(b) Closing of an microfluidic channel, Berdichevsky 2004.

Figure 1.5: different views of the conducting polymer microfluidic valve by Berdichevsky (2004).

$$PPy^+(DBS^-) + Na^+ + e^- \longleftrightarrow PPy^0(NaDBS) \tag{1.2}$$

The study of Berdichevsky shows how diverse most of the relevant state of the art topics are. The redox reactions, electrochemical polymerization, lithography, advanced materials, mechanical properties and microfluidics are all studies fields to gain more insight. This diversity needs to be taken into account in order to get a meaningful understanding of electrochemically expanding conducting polymer microfluidic valves. This is why the different topics are branched out in 3 parts that built up the knowledge, step by step. Section 1.1.2-1.1.5 will give an explanation of the material and its properties, the specific expansion reaction and an overview of applications and opportunities.

1.2. CHARACTERISATION: CONDUCTING POLYMER ACTUATOR

The next section will cover the design aspects of a Conducting polymer actuator, some of the different types of actuator designs will be discussed together with data on their properties and corresponding fabrication techniques. Next to electrochemically expanded conducting polymer actuators there are other promising designs like IPMC, piezoelectric, thermal, pneumatic electrostatic. These designs will not be discussed in this report.

1.2.1. CONDUCTING POLYMER ACTUATOR

A lot of research focuses on electrochemical conducting polymer artificial muscles. These actuators can be made in numerous ways. Some of the most important design choices will be discussed next.

TRANSFERRING EXPANSION TO ACTUATION

An important design choice in studying the expansion of the conducting polymer can be the principle in which the expansion is transferred into actuation. Figure 1.7 will show some different approaches to this problem.
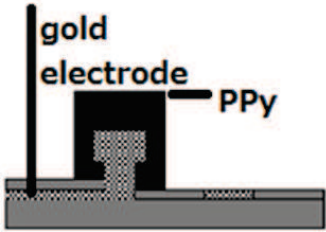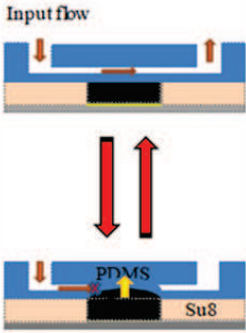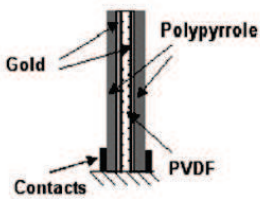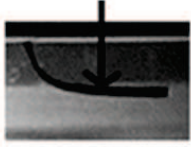
	example 1	example 2	example 3	example 4
Schematic	gold electrode PPy	Input flow / PDMS / Su8	Polypyrrole / Gold / PVDF / Contacts	1 layer of PPy
Study	Berdichevsky, 2004	Lefevre et al, 2008	Jager et al, 2000	Kaneto et al, 1995
Type of microvalve	direct actuation on piston	direct actuation	5 layer beam actuator	3 layer beam actuato
Working principle	anisotropic volume change of layer on protruded post	anisotropic volume change of layer	more-layer expansion bending	1 layer expansion bending
Length (µm)	110	>100	10.000	15.000
Width (µm)	110	>100	5000	1000
Thickness (µm)	34	50	170	25

Figure 1.6: Different approaches on transferring expansion to actuation [1], [13], [14], [15].

One principle is direct actuation of bulk material (first 2 examples on figure 1.7). Direct actuation usually consists of a conducting polymer layer on a non deform-able base layer. Due to this inactive layer the expansion of the material is the maximum actuation that is possible for this system. One of the ways to get the most expansion is shown in example 1 and 2 of figure 1.7, the relative special an-isotropic expansion of polypyrrole is used to get to an expansion of up to 30 percent [1]. This system is mostly fabricated by using lithography and can be used in micro or nano systems. The drawbacks of this system are the expansion which is limited to the layer thickness and, more importantly, delamination problems at the interfaces of expanding and non-expanding materials. One way to have less delamination is shown by the protruded post in example 1 of 1.7.

The most common actuation method is using bending beams of multiple layers, shown in example 3 and 4 in figure 1.7, using the principle of different expansions of well adhered material layers. When the layer of expanding conducting polymer expands, it will cause a bending in the direction of the inactive base layer. The advantages of these kind of systems are the easy mm-cm scale fabrication and delamination will be prevented

by the flexible base layer. The bending beam method has 2 variations.

The first variant (example 3 of 1.7) uses 2 layers of expanding conducting polymer which are situated on both sides of the base layer. Usually the conducting polymer is made by electrochemical polymerization. Electrochemical polymerization if performed on an electrode, this means an electrode must be added to the system on top of the base layer. This results in a 5 layer system, which is more complicated but has the advantage of having an active expanding and compression side of the beam, which will greatly increase the actuation speed or force. The base layer of this system can be used as a solvent reservoir if it is made of a porous material([16]). This will allow the system to operate outside of a solvent solution, since the ions will move through the reservoir from one conducting polymer layer to the other. The disadvantage of this system is the complexity and the presence of an electrolyte is still needed because of evaporation.

The second variant (example 4 of 1.7) uses 1 layer of expanding conducting polymer which is situated on an electrode on the base layer, making this a 3 layer system. This system is commonly made with a flexible base layer followed by an electrode and an electropolymerized expanding conducting polymer layer. This system has to operate inside of a solvent solution and due to its simplicity can be used in smaller systems and even in MEMS([17]). Another advantage of using 1 instead of 2 layers of expanding polymer is the Application in a microfluidic valve. The base layer can be designed to have specific properties like chemical resistance, flexible properties and act as a barrier for water and electricity. This can be an advantage when the baser layer is in direct contact to the controlled fluid inside a microfluidic system.

CONDUCTING POLYMER MATERIALS AND DOPANTS

Polypyrrole is used in most actuators. Other possible materials are poly-aniline [18])) which is only electro-active in solutions with a ph below 4)([19]) and polythiophene ([20]). The doping of the material has a significant influence on the characteristics of the actuator [21], it will also partly determine some of the structure of the polymer material, as can be seen in section 2.2.2.

Figure 1.8 shows 3 examples with 2 different working principles, the first 2 examples are the already introduced multi-layer bending beams actuators, the third system is made by lithography and consists of polypyrrole on top of a gold flexible electrode. The 3 systems differ when looking at the different dopants which are used during the electropolymerization of the active polymer layer. The third system, as shown in 1.8, is made with Sodium dodecylbenzene sulfonate (NaDBS) Dopant. This is the most commonly used dopant to make the polypyrrole with expanding properties. NaDBS is very stable, has some good mechanical properties, can expand up to 2-3 percent in all directions (with an-isotropic expansions of up to 30 percent) and is easy to use because of the better known characteristics.

The first system uses lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), this dopant is less commonly used, but according to Wu et al(2006)([16]) it will produce a system with larger or faster actuation responses than NaDBS. Wu et al also compared another dopant called hexafluorophosphate (PF6), this is shown in example 2. Hexafluorophosphate dopant has better characteristics than NaDBS . But compared to LiTFSI hexafluorophosphate has 35 percent less actuation, there are also a small number of studies that use this material as a dopant for polypyrrole.

Since there are no previous studies with exactly the same process and dimensions for polypyrrole actuators with NaDBS and LiTFSI, this research will look at the actuation frequency. Wu et al reported of a 1 hz actuation (0.05M LiTFSI and 1V) with a maximum deflection. Berdichevsky et al [1] reported a time of 10 to 15 seconds for maximum deflection(0.01M NaDBS and 1 V).

Most studies use the dopant solution in both the polymerization phase and the actuation phase, but always without the monomer during actuation. The electrolyte concentration [8] and the electrolyte itself also affect the properties of the expansion. Jafeen et al [22] reported on Lithium chloride salt being a better ion carrier than the most commonly studied sodium ion containing salts. This was mostly because of the good hydration number, this hydration number relates to the osmotic side effect of water moving into the matrix of the polymer materials. Matinez et al [8] found the optimal solution of Sodium Chloride (NaCl) electrolyte of 0.3M. The most commonly used concentration of LiTFSI is around 0.05, mainly because of its limited solubility.
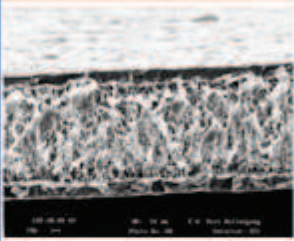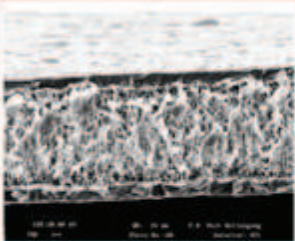
	example 1	example 2	example 3
Schematic			
Study	Wu et al, 2006	Wu et al, 2006	Jager et al, 2000
Type of microvalve	5 layer beam	5 layer beam	patterned layers
Working principle	more-layer expansion bending	more-layer expansion bending	bending through expansion
Length (µm)	10000-40000	10000-40000	50-300
Width (µm)	2000	2000	20
Thickness (µm)	140	140	1,5
Deposition	electropolymerization	electropolymerization	electropolymerization
Conducting polymer (mol)	0.06 M pyrrole	0.06 M pyrrole	0.1 M polypyrrole
Dopant (mol)	0.05 Li+TFSI−,	0.05 TBA−PF6	0.1 NaDBS
Electrode	gold	gold	gold
Deposition time	12hr (0.10 mA/cm2)	12hr (0.10 mA/cm2)	0.1mA/cm2
Thickness layer (µm)	15	15	1
Solvent	propylene carbonate	propylene carbonate	water
Electrolyte (mol)	Li+TFSI−, 3M	TBA−PF6	NaDBS (0,1)
Voltage (V)	1v	1v	0,5 to 0,6
Speed	1Hz to 10 hz (62mm - 5mm)	1Hz to 10 hz (22mm - 2mm)	2sec
Force	1,2mN	0,8mN	not available
Expansion	65mm (40mm actuator)	22mm (40mm actuator)	180 degrees

Figure 1.7: Different approaches on dopants used for the expansion properties of polypyrrole [16],[16], [17].

ELECTRODE MATERIAL

Most of the systems use gold or platinum as an electrode in de electrochemical deposition of the expanding conducting polymer. Gold and platinum can be sputter coated onto a surface. Another electrode material that is not yet used as an electrode for electropolymerization of expanding conducting polymers is poly(3,4-ethylenedioxythiophene) (PEDOT). However it is already used in a lot of electrode applications like light emitting diodes(LED) [23], Organic solar cells [24] and touchscreens [25]. This PEDOT conducting polymer has many advantages. Unlike gold it can easily be spin coated on top of a surface, it is more flexible than metals and there are multiple ways of patterning the PEDOT without needing a clean room for lithography. Ways of patterning PEDOT include spin coating on a plasma-treatment-patterned surfaces, ink-jet printing, screen printing or even soft and hot/soft embossing.
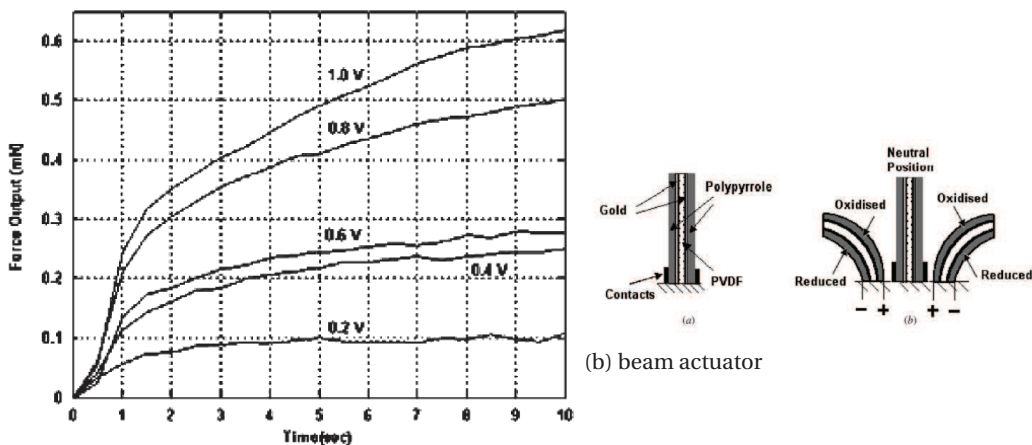
(a) Force of a 5 mm conducting polymer actuator doped with
LiTFSI

(b) beam actuator

Figure 1.8: Data on conducting polymer beam actuators that operate in 'air', Alici 2009 [26].

ACTUATION

Gursel Alici et all show [26] that it is possible to make a conducting polymer beam actuator that operates in air. There is still a need for an electrolyte solution in the porous membrane of the actuator, this can be accomplished by soaking the beam in a solution of a salt that contains sodium, lithium or another suitable positively charged ion (cation). Figure 1.9 shows the forces, voltages and time periods of a 5 layer PPy-LiTFSI actuator. It can be seen that the actuation forces are relatively small, but the big actuation should be used to close a relatively small microfluidic channel. A possibility can be to increase the pressure when using the big actuator and focusing this force on a small surface. Section 1.3.2 will focus on the implementation of actuator in microfluidic valves.
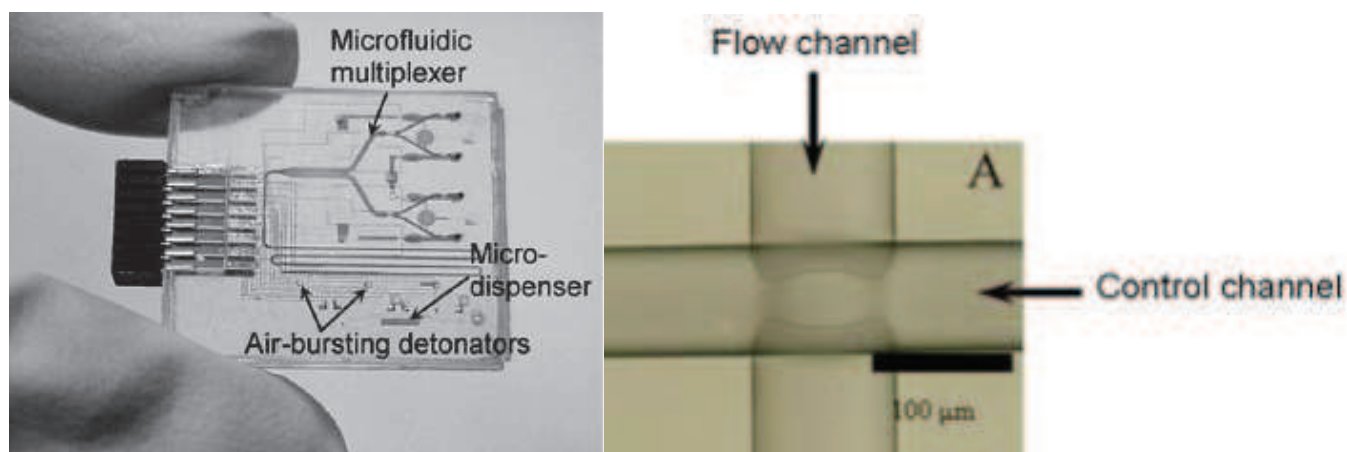
(a) smart Lab on chip, Ahn 2004   (b) Quake valve [27]

Figure 1.9: Two application of microfluidics that show a complex lab in a chip (figure a) and a well known Quake valve(figure b), traditionally used for experimental microfluidic valves.

1.3. APPLICATION: CONDUCTING POLYMER MICRO VALVE

The next section will cover the numerous aspects of a Conducting polymer micro valve working in a microfluidic system. Some of the different aspects of microfluidics will be discussed first. Subsequently there will be a discussion about combining all the aspects of polymers, conducting polymer actuators and microfluidics.

1.3.1. MICROFLUIDICS

Microfluidics is the field of study that looks at the fluids inside systems with micrometer size features. Some of the key applications of microfluidics are the ink-jet print-heads and Lab On Chip devices (LOC) (see figure 1.10a). The two main advantages of microfluidic systems are the small amounts of fluids which are required and the scaling phenomena that occur and can have a good effect on the sensing ability of electrochemical processes.

LAB ON A CHIP

Some studies focus at making small microfluidic systems that can perform medical tests. These systems can be called Lab On Chip devices and can be used in medical tests and in some cases they can be used as disposable medical testing equipment. figure 1.10a depicts a smal LOC system in which small microfluidic channels connect to multiple parts of the system. These special parts of the system can manipulate, sense or actuate the fluids that pass through it. Already a lot of research was done on making sensors for the LOC systems. (conducting) Polymers are widely used to sense ph or other processes in which electron transfer must be measured. Some research is also done on making mechanical manipulators for these systems, these include micro valves and micro-pumps.However these studies did not focus on expanding polymer systems. One of the most widely used materials in microfluidics is PDMS. The advantages of PDMS are the transparent optical properties, it is bio-compatible, easily deform-able, inexpensive, easy fabrication and it can make easy bonds with glassware by plasma treatment. Another material that is well suited for microfluidics is the Cyclic co polymer from TOPAS, this transparent material has more strength and good defined transition temperatures. This TOPAS material can be used as a flexible, but strong, base layer. This layer can be used as a separation layer between the microfluidic side of a system and the electrochemical reactions of the actuator side of the system. Together with the PPy actuator this will allow for precise electrical measurements in a LOC device, without the influences of unwanted electrical signals, chemicals from the actuation of PPy, heating elements or electrical noise from high voltage actuation.

QUAKE VALVE

One of the most used microfluidic valves is called the quake valve 1.10b, which is designed by Quake, Hosokawa and Maeda (2000). The quake valve offers a commonly used method for making a fast and easy microfluidic valve. It is operated with pneumatic pressure on 1 micro channel that is situated under or above a fluidic micro channel. The 2 channels are separated by a thin layer. This thin sheet of material can expand into the

(a) Normally closed valve by Li et al. [28]

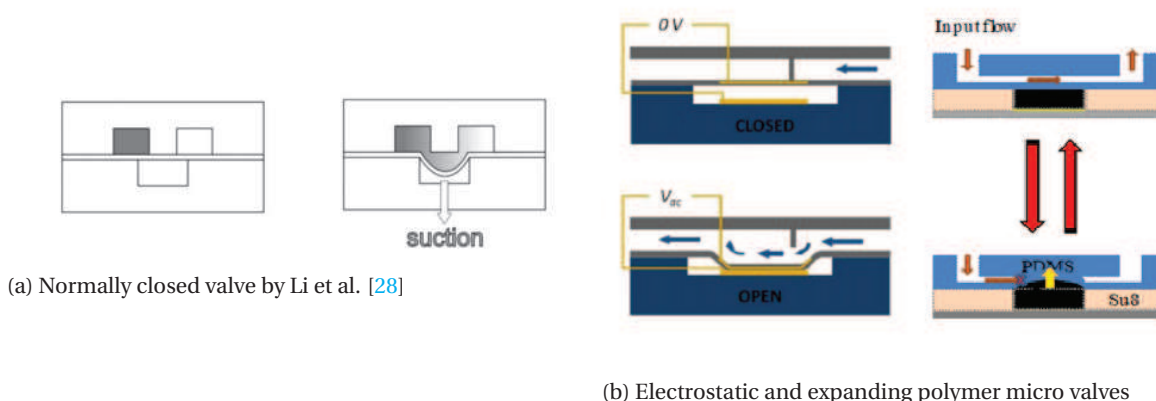(b) Electrostatic and expanding polymer micro valves

Figure 1.10: Three examples of different microfluidic valve. Figure a shows a pneumatic valve, actuated by applying a vacuum on an additional chamber. Figure B shows an electrostatic system on the left, two conducting surfaces attract each other with a high electric potential, this will open a valve. The last image shows an expanding conducting polymer system, expansion will push to close a flexible PDMS channel

fluidic channel if a pneumatic pressure is applied, which will close the microfluidic channel. Besides this normally open system there are also systems that are normally closed and opened with a vacuum(see figure 1.11a) Some of the advantages of these micro valves are the speed and reliability. A big disadvantage however is the need for compressed air. This compressed air will make the system reliant on big compressor. This is why there are some studies to make alternative methods of closing of a micro valve (see figure 1.11b). The first system [29],see figure 1.11a, is an electrostatic mechanism that is used to open a normally closed valve with the use of a high voltage(around 60 V) that attracts the actuating mechanism. The normally closed design can be used for a conducting polymer microfluidic valve. The second system [1] ,see figure 1.11a, uses the direct an-isotropic expansion of polypyrrole to close a microfluidic channel. The actuation of this system is the direct swelling of a thick block of PPy. This block of PPy can be replaced by a thin layer of PPy when a proper system is designed in which a large beam of material can produce a localised force to close a smaller channel. The advantages of these systems are the possibilities to make the system portable, the disadvantages of both systems are the complexity of the fabrication, in which clean rooms with lithography are used.

1.3.2. DESIGN: CONDUCTING POLYMER MICRO VALVE
The previous sections provided insight into different disciplines which are essential to understand when researching and designing the conducting polymer microfluidic valve. This knowledge can be used as the basis for improving the existing conducting polymer microfluidic valves design. In order to improve the existing designs, knowledge gaps have to be identified and researched in order to come to a new and improved designs.

The design that is proposed in this section is chosen to best include the opportunities that were discussed earlier. To get an overview and keep the project in the right time-frame, the main focus of this project is the fabrication of an all polymer actuator that eventually can be included into a microfluidic system. Important design aspects will be developed with and without the support of available literature examples. Minor aspects are based on the amount of the available literature studies. The most important of the design aspects are the flexible layer of TOPAS, the PEDOT electrode with the active layer of PPy and the possible implementation of the actuator in a microfluidic system. Section 1.2.1 discussed 2 types of expanding conducting polymers actuators, the direct actuation and the beam actuators. The direct actuator has been used in multiple microfluidic systems([1] [13] [30]) but the beam actuator was not yet used as a microfluidic valve, even though there is much more attention for this type of actuator in other applications. One of the gaps in the current knowledge is that there is little insight regarding the use of conducting polymer beam actuators as microfluidic valves in microfluidic systems. This knowledge gap can be overcome with the insight that replacing the pneumatic part of the Quake valve by a simple beam actuator that is situated on top of a thin film . This film can replace the thin film from the quake valve and use the pneumatic channels for the electrolyte supply. This design replaces the compressors by small batteries or power supplies with minimal design changes compared to the quake valves. The commonly used material polypyrrole can be electrochemically deposited

on a layer of a polymer electrode, likely PEDOT. This layer can be designed in such a way that it can bend or buckle between 2 positions when a current is applied. The polypyrrole will be doped with the commonly used dopant sodium dodecylbenzenesulfonate, NaDBS or LiTFSI with better characteristics. The ion delivering electrolyte for the expanding conducting polymer will be NaDBS or LiCl. The valve will also consist of multiple layers of soft and transparent PDMS or TOPAS material that can be made using soft lithography. The following sections will discuss multiple fields of knowledge that can be taken into consideration in order to improve conducting polymer microfluidic valves.

Actuation speed

The traditional pressure actuated microfluidic valves [31] use high pressures to make fast actuation possible. One of the disadvantages of expanding conducting polymer is the slow expansion rate of 10 to 15 seconds [1, 14] before an expansion percentage of the desired effect can be reached. Faster actuation will make the design suitable for more applications and can be accomplished in a number of ways. Dimension and specifications (such as the electrical active surface area, temperature, electrolyte concentration, type of electrolyte, ph, solvent and concentration of active centers in the film) can be optimised to reach a faster actuation speed [8, 32–34]. Another possible improvement can be made by using the change in stiffness instead of the expansion of the conducting polymer[35]. Some studies show that the expansion of conducting polymer is driven by 2 different reactions. The first reaction can change the stiffness up to 20 times faster than the change in length [36–38].

bio compatible, all polymer design

Conducting Polymers have two useful characteristics and therefore can easily be used to close microfluidic valves. These characteristics are the low voltage actuation and the organic nature of polymers. These two characteristics can be used to differentiate the conducting polymer microfluidic valve from the already existing designs. common used micro actuation designs often use a combination of non-bio compatible metals , high voltages[29, 39], high pressures [31] or high temperatures[40]. A bio compatible micro valve can be made if the commonly used gold [13, 41–43] or platinum[14, 26, 44] electrodes are replaced by another (non)expanding conductive polymer like PEDOT[45].

Delamination and lifetime

Delamination of the expanding conducting polymer is a common problem when working with relative thick layers of expanding material[13]. Luckily there are multiple existing techniques to minimise delamination. A protruded electrode post can be used to be deposited with expanding conductive polymer[1] or a long and relative thin beam of electrode and expanding conductive polymer can be used[26]. Longevity of the micro valve is important in some applications, fast alternating motions can make the valve delaminate or break too early. A small life cycle will rule out the usage of conducting polymers in several applications.

Low power shape locking

The volume change of the conductive polymer is a reaction powered by a current. When withholding the current to flow, the expansion will not instantly move back to the starting position*. This principle, together with the faster stiffness change, can be used to make interesting designs such as bi-stable beams that, when properly designed, can quickly balance between an open and a closed valve position. This will make fast actuation possible, together with a small current, that is only consuming power when changing position.

Portability and Modularity

The low voltage requirements for the actuation of conducting polymer allow for system designs that use small batteries as power supplies. This can open the way for more advanced portable, low costs, lab on chip devices that can be used outside of a laboratory. Modularity has to be investigated to ensure compatibility with existing techniques to make lab on a chip devices. An example is the use of the basics of a quake valve, this system is already widely used and with a simple modification the thin separation layer can be replaced by a thin layer that can actuate without external pneumatics. Another big improvement can be the patterning of active PPy parts on the thin separation layer. This will open up opportunities of using multiple microfluidic valves, multiple clustered valves to become a pump and other active or sensing parts

2

CONDUCTING POLYMER SYSTEMS

2.0.3. INTRODUCTION

The different aspects of the conceptualisation and creation of an all polymer conducting polymer microfluidic valve are described. Conducting polymers have great potential in numerous applications and are rarely used in microfluidics. The all polymer actuator, see figure 2.1 can eventually form the basis for new opportunities regarding the miniaturisation and commercialisation of Lab on Chip devices. Active components can be powered by miniature batteries instead of pressurised air.

A new approach of using Conducting polymer actuators as microfluidic valves is presented in this chapter. The new method uses the widely known multi layer bending beam actuator, commonly used as an artificial muscle or soft actuator. The system will directly replace a thin separation membrane of traditionally used microfluidic Quake valves by an active thin layer. The active part of the system is a layer of doped polypyrrole(PPy) which shows expansion after a reduction reaction. The actuation of the all polymer system is the result of a multi layer system, when one of the active layers expands a bending moment will be created. The design and characterisation of the different layers of the system are described. The layers include a support substrate, a flexible layer of TOPAS, the PEDOT-based electrode and the active PPy layer doped with NaDBS or LiTFSI.

Figure 2.1: Active layers of the all conducting polymer microvalve actuator systems.
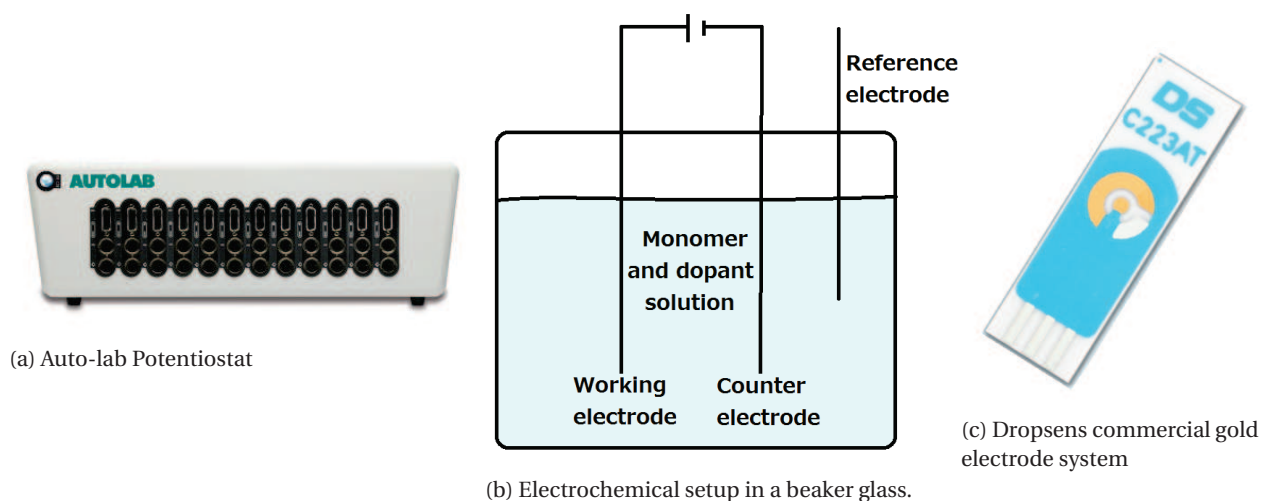
(a) Auto-lab Potentiostat

(b) Electrochemical setup in a beaker glass.

(c) Dropsens commercial gold electrode system

Figure 2.2: Three important setups for performing the electrochemical experiments.

2.1. METHOD AND MATERIALS

Polydimethylsiloxane (PDMS)(Dow Corning Sylgard 184 - pt A / pt B) was initially used for the base material of the design. This silicon based polymer is commonly used in microfluidics to build systems with micro channels. One of the advantages is the easy fabrication with a liquid gel like polymer that is hardened into a transparent elastic material, it can copy high resolution details as a mould when hardened using a curing agent. PDMS is gas permeable and has bio compatible characteristics. The PDMS was first degassed before making thin layers in the spin coating process. TOPAS was eventually used because the PDMS could not meet the design requirements.

TOPAS (TOPAS Advanced Polymers, 3 mm granules of TOPAS® 8007X10) is the trade name for TOPAS Advanced Polymers cyclic olefin co-polymers and can be used as an alternative to PDMS. TOPAS is a co-polymer and consist of a mixture rate of Ethylene and norbornene. The material is stronger and more stable than PDMS. It is also more chemically resistant and can be bio compatible in some cases. TOPAS is used for the base layer of the system. TOPAS acts as a non-conducting and non porous thin layer that can replace the PDMS membrane of a microfluidic Quake valve. The base layer is used as 1 part of the bi-layer bending mechanism. If one of the layers expands, there will be stresses in both bonded layers that will causes the system to bend.

The substrate has to satisfy some requirements for the design of the system. The most important requirements are the material properties. A thin layer of material is the basis of the system, this layer must have enough strength to be easily handled in the fabrication. Besides the strength it must remain flexible or thin. The material is also required to have some ability to allow adhesion of the PEDOT electrode material. TOPAS can be dissolved in toluene and be spin coated to match the required film thickness, ranging from 1μm to over 100μm with multiple layers [46].

An ultrasonic cleaner was used to dissolve TOPAS into toluene. The toluene and TOPAS granules were put inside a glass beaker and subsequently the ultrasonic waves and heating caused the granules to dissolve into the toluene. The toluene-TOPAS mixture was stored in a refrigerator.

The thin flexible layer of TOPAS was spin coated using a Dimensions Polos spin150i-2 spin coater The spin coating process was characterised by the spin speeds in rounds per minute (rpm), acceleration (m/s2) and time(s). These settings can influence the thickness and uniformity of the coatings. Another way of coating a surface is using gravity to drip-coat a surface. The entire surface was covered with the required material and held at an angle, removing the excess material. This method was used for making test samples when the thickness of the sample had no influence on the experiment.

Polypropylene (PP) and glass was used as the temporary substrate. The smooth side of the samples, that

are in contact with the PP or glass were used for the deposition of the following layers. Polypropylene (PP) sheets were used as a chemically resistant layer for spin coating TOPAS toluene solutions. PP-TOPAS layers were cut into shapes before or after experiments. After the evaporation of toluene the layers of TOPAS the PP layer were used as support or removed. The extra layer of PP offers rigidity, but stress was built up in the TOPAS if it was removed from the PP. These stresses during removal were the result of stretching by adhesion forces. Before the deposition of the next layer the contaminants from the surface were removed with isopropanol cleaning and plasma treatment(Diener Femto). The oxygen gas plasma was performed in a vacuum for 2 minutes at 60W. The surface becomes hydrophilic due to the introduction of polar functional groups[47], this allowed for the adhesion of the PEDOT-PSS electrode material.

The electrode had to satisfy requirements to facilitate the electrochemical deposition of the active PPy layer. The main requirements were the adhesion properties to the TOPAS base layer and the facilitation of the electrical conductance for the PPy deposition. Poly(3,4-ethylenedioxythiophene) (PEDOT) is a promising conductive polymer that is widely used to make surfaces electrically conductive. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT-PSS) (Sigma-Aldrich 1.3 wt percentage dispersion in water) is used, PSS allows the material to exist in a liquid. This liquid was spin coated on top of the plasma treated TOPAS to form an electrode for the polymerisation of PPy. Isopropanol was added for better wettability properties, which produced better spin coating results[48]. Polymerization of the active part of the actuator took place in a solution, which formed a problem when the initial untreated PEDOT solution was dissolved in water. To counteract this problem ethylene glycol (EG) was used in the solution of PEDOT-PSS [2]. The same principle is also reported to work with a surface treatment of an EG bath [49]. Ethylene glycol(EG) was also used for better conductivity. A composition of PEDOT-PSS:IPA:EG of 100:20:5 was used. The concentration of IPA and EG were derived from other studies [48][2]. The PEDOT-PSS:IPA:EG[100:20:5] layer was further called PEDOT layer. The PEDOT solution was spin coated on top of a TOPAS surface. After drying a solid and conducting layer was left.

To measure the conductivity of the thin films of PEDOT, a 4 point probe (signatone) with 62.5.mills (1.5875mm) spacing was used. A Keithley 2400 source meter and keithley 2182 nanovolt meter were used for the current supply and voltage sensing. The conductivity versus thickness of multiple PEDOT layers was measured on different places on each electrode.

Pyrrole (Sigma-Aldrich, reagent grade 98 percent monomer) wa used to make polypyrrole layers of active material. Pyrrole was dissolved in water during electropolymerization together with a Dopant salt. A total of 2 commonly used dopants was used.

Sodium dodecylbenzenesulfonate (NaDBS) (sigma aldrich, salt) was used as a dopant. NaDBS is widely used in the polymerization of PPy because of the stable characteristics. Electropolymerization will produce long chains of DBS, entangled in the matrix of the polypyrrole. Advantages of NaDBS are the number of available procedures for electropolymerization together with PPy.
Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) (sigma aldrich, salt) was the second dopant. NaDBS is more commonly studied, but LiTFSI can deliver faster actuation speeds and better displacements than NaDBS dopant.

The potentiostat (Metrohm Autolab M101 multi-channel potentiostat with Autolab Novo 1.10 software), see figure 2.2a,is an important device for the polymerization of PPy and the electrochemical characterisation of conducting (expanding) polymers. The potentiostat system applies different electrical signals between electrodes and accurately measures the electrical response by using a reference electrode. The sample was the working electrode, a piece of aluminium was used as the counter electrode and a silver electrode (Dropsens) was used as a reference electrode, see figure 2.2b for a schematic view. This silver electrode had have a known electrode potential that would allow the system to measure a more accurate representation of the actual potential over the system.

Figure 2.2c shows the commercially available screen printed electrode from Dropsens (DRP-C223AT) that was used. The working electrode (diameter of 1.6 mm) and counter electrodes are made of screen-printed gold, the reference electrode was made of silver.
The test setup in combination with the potentiostat was used to perform polymerisation, actuation and measurements such as amperometry, voltammetry and cyclic voltammetry.
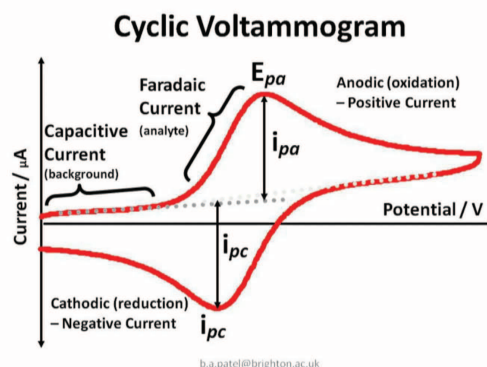
Figure 2.3: Representation of typical cyclic voltammetry plot, including the most important parameters.

Cyclic voltammetry was used to characterise the polymerisation of the PEDOT and PPy layers. Cyclic voltammetry is a procedure in which the current flow under a triangle wave voltages is measured in a specific change in voltage per second (scan rate in [V/s]). This will show properties such as the oxidation (E_{pa} and E_{pa}) and reduction peaks (E_{pc} and E_{pc}), the capacitive currents and the Faradaic currents, see figure 2.3.
A reversible electrochemical reaction shows 4 distinct characteristics:

- Voltage separation: $\Delta E = E_{pa} - E_{pc} = \frac{59}{n} mV$ with n being the number of electrons involved in the redox reaction

- No change in peak voltage with a different scan rate

- Both peaks have the same absolute magnitude

- The magnitude of the peaks are proportional to the square root of the scan rate

Amperometry was used to polymerise materials at a set voltage. During this operation the current was measureded. The measured current during the electropolymerization is related to the amount of electrons used in de polymerisation. The total mass was calculated by integrating the current over time. Polymerization of polypyrrole at a given potential can prevent the over-oxidation of PPy. To prevent over oxidation a cyclic voltammetry measurement was used to see the over oxidation potential. Over oxidation will make a sample of expanding conducting polymer non conducting and inactive.

Potentiometry is similar to amperometry. The Current was set at a constant, this will have a constant rate of polymerization with a changing voltage. Over oxidation can occur when the polymerization potential reaches the oxidation potential of water at around 1V. The mass of the material was derived from the time and constant current.

A Jeol JSM-6010LA scanning electron microscope was used for looking at the morphology of the polypyr-role layers. The SEM was also used for checking the thicknesses of the layers.

The Quorum Technologies SC7620 sputtercoater was used for making thin layers of gold electrode material on top op TOPAS. These gold electrodes were used to compare to the PEDOT.

2.1.1. ACTUATION
The actuation is estimated by the tracking software KINOVEA. The KINOVEA software uses the recorded video of the MOTICAM 5.0 attached to a Motic microscope. Figure 2.4 shows the experimental setup on the left and the begin and end-frame taken from microscope video on the right. The expected displacement can be calculated using Timoshenko's model shown in figure 2.1. This equation is used for bi layer bending due to differences in coefficients of thermal expansion. The thermal expansion is replaced by 2 percent redox expansion of polypyrrole, commonly achieved in literature [1].

Figure 2.4: Experimental setup of a TOPAS-gold-PPY/NaDBS actuator beam,designed to measure the displacement at micro scale.

$$\frac{1}{R} = \kappa = \frac{(\alpha_1 - \alpha_2)}{h_2} * \frac{6mn(1+m)}{1 + 4mn + 6m^2n + 4m^3n + m^4n2} \qquad (2.1)$$

Figure 2.5 shows the contours of the expected bending, calculated with Timoshenko's model for bi-layer bending. This equation uses the difference in the coefficient of thermal expansion of 2 well adhered layers. The thermal expansion is replaced by the expansion caused by the swelling of the PPy layer. The contours represent the expected displacement of an actuator (fully submerged) in a liquid, with a total active length of 1 cm. The actual actuator will be recently submerged, together with a droplet of electrolyte at the base of the 1 cm actuator. The red dot (surrounded by the measurement error) will represent the calculated expected result if there is 2 percent expansion. A 10 mm long test sample with a radius of curvature of 5 mm will bend 113 degrees around a 5 mm circle. This will result in a tip displacement of around 13 mm.
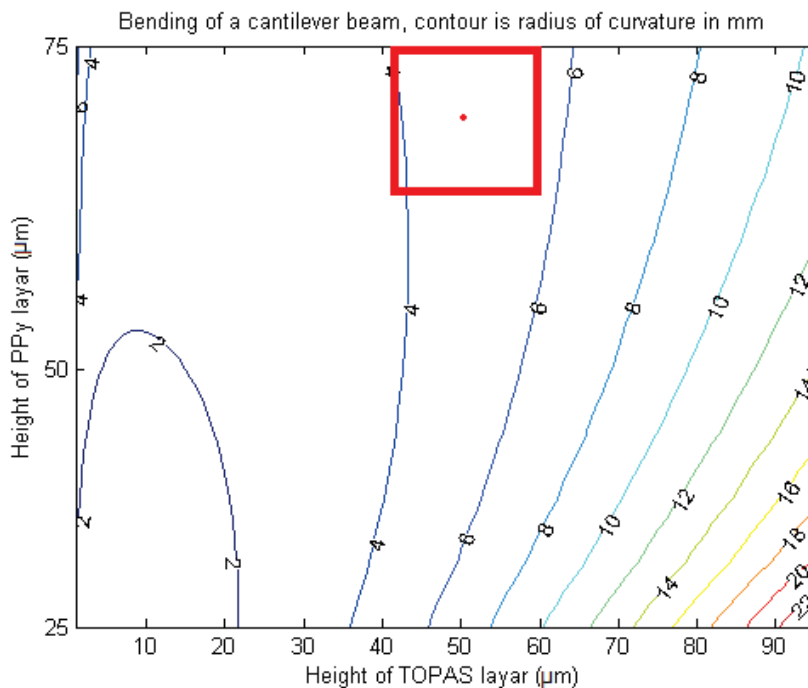

Figure 2.5: Contours of expected bending. The red dot at 50 μm thick TOPAS and 70 μm thick PPy indicates the maximum curvature for an expansion of 2 percent, calculated using Timoshenko's model for bi-layer bending.

2.2. RESULTS AND DISCUSSION

The Results and discussion section will show the design process of the conducing polymer microfluidic actuator system, together with the characterisation. After setting requirements for each part of the system a design is made based on literature and experiments. After fabrication the design is characterised and the results are discussed. In the case the design does not meet the requirements, literature will be used in order to find the underlying principles that can be used to improve or study experiments.

The start of the design is the fabrication of the base layer, this substrate will have to comply with different requirements such as layer thickness, strength and adhesion properties. Some of these requirements are specific for the interface between the base layer and the electrode layer. The design of the Electrode layer will be the next step. The adhesion properties and the electrical conductivity are required for the base layer. This layer has interfaces with both the active layer of polypyrrole and base layer of TOPAS. The deposition requirements of PPy are the variable layer thicknesses and the adhesion properties. The layer will be exposed to bending and needs to be connected to the other layers for actuation. The experiments for actuation of the active layer of polypyrrole will be discussed last. Requirements for the actuation are the common literature expansion of 2 percent and a response time in the order of a second.

2.2.1. SUBSTRATE AND ELECTRODE

	Layer thickness [μm]	PEDOT (+EG) adhesion (M)	PEDOT (+EG) adhesion when submerged (M)
PDMS sheet	≈ 200 (L)	x	x
PDMS thick spin coated	>2500 (M)	0	x
PDMS thin spin coated	<100 (M)	0	x
TOPAS sheet	300 (L)	0	0
Liquid TOPAS spin coated	20-35 (M)	0	0
Liquid TOPAS drip	≈ 35 (M)	0	0
Layered liquid TOPAS	20.0- >100 (M)	0	0

Table 2.1: Summary of different substrates experiments (M = manually measured with 10 μm maximum error, L = supplied by manufacturer or literature, x = does not pass initial requirement, 0 = passes initial requirements)

SUBSTRATE
Table 2.1 shows the different materials that were compared in order to design the flexible substrate layer. The idea of using PDMS was first tested on commercial PDMS Sheets, thick PDMS layers and custom spin coated thin layers. PDMS is a hydrophobic material and needs a oxygen plasma treatment to become temporarily hydrophilic to allow for spin coating of the PEDOT that is supplied in water solution. The first PDMS sheet was supplied in a large roll of ≈200 μm thick material and had a large surface roughness. Initial test of adhering PEDOT on the plasma treated surface were therefore ascribed to roughness and further PDMS test were performed. To decrease the surface roughness, thick(≈ 2500 μm) and thin(<100μm) samples of spin coated PDMS were fabricated. The spin coating process showed a visible smoother surface, these samples resulted in a PEDOT-PSS layer that showed promising initial adhesion properties. To further test the adhesion the PDMS-PEDOT samples were submerged in water, as the layers of PPy will polymerise when the system is submerged in liquid. This submersion resulted in a direct delamination of the PDMS and PEDOT. After improving the PEDOT layer fabrication protocol with the addition of EG and IPA the layers still did not meet the design requirements. There are various literature reports on the use of PEDOT with PDMS surfaces. Spin coating PDMS on a stretched sample of PDMS [50], incorporating PDMS into an aerogel of PEDOT-PSS [51] and using ink-jet printing of PEDOT on PDMS [52]. Literature would suggest the possibility of improving the adhesion of PEDOT on PDMS for meeting the design requirements, this was not continued because of other disadvantages of PDMS. One of this disadvantages of PDMS was the low strength of around 6.7 MPa [53] this would have resulted in a more complicated fabrication process when working with thin layer of PDMS with thicknesses of less than 100 μm. other disadvantages were the structural stability over longer periods of time

and the high diffusion of water molecules into and through the material[54].

Instead of PDMS, TOPAS was tested and used as the thin substrate material. The material was already available from research of soft embossing PEDOT on TOPAS [55]. This soft embossing can also be used to pattern a PEDOT-TOPAS system before the polymerization steps occur. Unlike PDMS, TOPAS has a good strength of around 2600MPa [56], this would allow for the fabrication of thin layers of less than 100 μm that were still easy to handle in the fabrication of the whole actuator. TOPAS sheets of 300 μm were first used to test the adhesion of spin coated PEDOT-PSS-EG-IPA on TOPAS, these experiments showed good adhesion of PEDOT on TOPAS. Due to the high strength of TOPAS the commercially available sheet of material was too strong to use as a flexible layer. In order to make an actuator with the thickness range of 20 to 150 μm the fabrication of liquid TOPAS was studied. The dissolved TOPAS-toluene (85:15 ratio) solution was spin coated to form layers of 20-35 μm. Variations of the spin coating variables such as the rotation speed, acceleration and duration could change the thickness of the TOPAS layer. The thickness of the TOPAS showed a small variation over the different samples. This was due to the non-homogeneous thick solution of TOPAS-Toluene at 15 percent TOPAS. Using lower concentrations of TOPAS would result in more reproducible results, but would produce layers with an undesired thickness. The spin coating of TOPAS-Toluene was replaced by the Gravitational dripping technique because of the more accessible fabrication and the need for less safety precautions regarding the use of Toluene. The Gravitational dripping technique was used to make big sheets of TOPAS with thicknesses between 35 and 60 μm, the produced layers had a bigger variation in thickness than the spin coating process. The design of the bi-layer actuator required a thicker layer of flexible substrate. This was accomplished using multiple layers of TOPAS that were stacked in order to make thicker sheet samples. This layered liquid TOPAS was chosen for the design. Polypropylene, glass, aluminium tape and Petri dishes were considered for designing temporary substrate for the deposition of TOPAS. Glass was used for the design because of the best properties including little adhesion to the TOPAS Layer. Polypropylene (PP) was a good base material because the PP-TOPAS could be cut into a required shape and this would result in a PP-TOPAS sample that is easy to handle during the following fabrication steps. The various TOPAS layeres were all tested for the adhesion of PEDOT-PSS-EG-IPA. All the layers showed a sufficient adhesion after applying oxygen plasma treatment for decreasing the hydrophobicity. These experiments were targeted at the adhesion of 1 layer of PEDOT, multiple layers were later discovered to form some problems. Possible treatments to increase the adhesion include decreasing the surface roughness during the liquid phase using flat stamps [46], or using a low roughness spin coating surface. Optimisation of the plasma etching could also affect the adhesion properties of the TOPAS. Optimising the plasma etching could change the number of acquired oxygen containing polar functional groups that provide the bonding of the liquid solution to the TOPAS [57]. A small experiment was performed to increase the adhesion by applying a extra coating of a rubber material to the TOPAS layer. This rubber layer showed good adhesion to the TOPAS and to the PEDOT without the need for oxygen plasma treatment. This method was not further investigated because the rubber layer did not have a good chemical resistance and the plasma treatment already showed sufficient adhesion properties.

PEDOT ELECTRODE

The investigation of the electrode layer started after the completion of the design of the TOPAS layer using multiple drip coated layers of TOPAS-Toluene on top of a glass substrate. The design of the electrode layer started with the investigation of the PEDOT-PSS treatment procedures and electrical resistance measurements on the electrodes. A comparison was made between the effect of an EG after treatment bath versus EG directly in the PEDOT-PSS-IPA solution. The EG bath had a slightly larger effect on the conductivity. The EG after treatment bath was not continued since a lot of defects occurred when multiple layers of PEDOT-PSS were spin coated on one sample. The treatment of PEDOT-PSS with different additives is studied in various studies. Pre-treatment with various additives showed that EG pre-treatment combined with a EG post-treatment had good results [2], this study also indicated that multiple layers can also improve the conductivity of a thin layer. The addition of a high boiling solvent like EG has an effect on re-ordering of the PEDOT-PSS chains and has the effect of increasing the conductivity and becoming insoluble in water. This is believed to be due to the changes in the polymer chains, these chains change from a coil to linear or expanded-coil structure [58].

Initially PPy polymerization tests with PEDOT electrodes showed that lowering the electrical resistance of the thin PEDOT layer had a positive effect on the polymerization speeds. This indicated that the electrical resistance (measured with a 4 point probe) of the thin films determined the deposition speeds when the

impedance of the PEDOT electrode was the limiting factor in the electrochemical process. The increase in conductivity was accomplished by applying multiple layers of treated PEDOT. This did not increase the overall conductivity of the PEDOT material, but the thickness would allow for the lower electrical resistance. The increase in conductivity of the thin layer was investigated by performing experiments with increasing the amount of PEDOT layers. Figure 2.6 shows the increase in conductivity versus the amount of spin coated layers. The next section will discuss the effect of this on the polymerization speed. Figure 2.6 shows the increase of conductivity of the thin films of multiple layers, the conductivity will increase almost proportional to the number of layers of PEDOT. The error bars indicate the highest and lowest values of 21 measurements on 3 different spots on 1 sample, the point between the error bars is the average film conductivity.
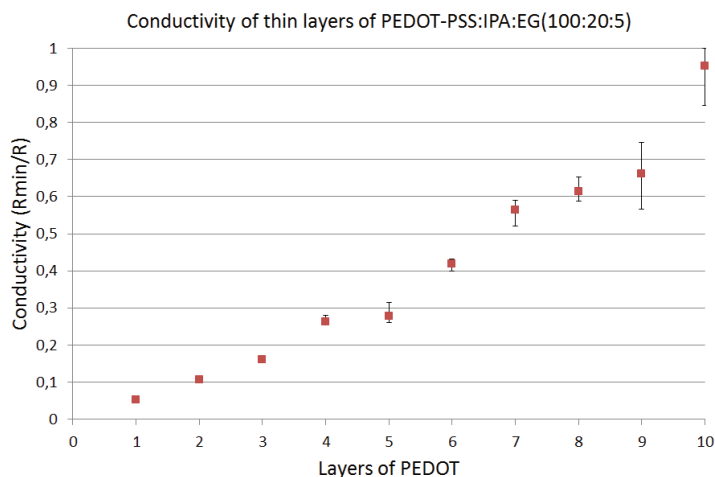

Figure 2.6: Effect multiple layers of PEDOT on the thin film resistance, there is an increase in conductivity for each added layer of PEDOT.

A similar increase in conductivity was also observed in electrodes of varying thicknesses of sputter coated gold electrodes. Gold electrodes were made with 10, 20, 30 and 40 nm gold layers. For the further design of the actuator most of the electrodes were made using PEDOT electrodes with a conductivity similar to the 5 or more layers from this experiment. Using other spin coating speeds could allow 3 layer PEDOT electrodes to have the same conductivity/thickness. The used material for spin coating was PEDOT/PSS-IPA-EG (in a 100:20:5 proportion), each layer was dried for more than 30 minutes at 60 degrees Celsius. This method still required attention because imperfection could start delaminations during spin coating.

Figure 2.7 shows the cyclic voltammetry graph of multiple layered PEDOT electrodes in NaDBS solution, this graph shows some of the chemical properties of the PEDOT electrode. The electrodes have a submerged surface of 0.5 cm^2, the scan rate was 0.01 V/S. The most prominent feature of the figure is the increasing currents for the 3 and 4 PEDOT layers, compared to the 1 and 2 layer PEDOT electrodes. This difference was also clear when conducting polymerization experiments, the 1 and 2 PEDOT electrode systems showed no visible PPy mass build-up. The reason for the low currents is also visible in the oxidation peaks of the 4 CV graphs, the reaction is slightly limited by the impedance of the system. Other systems could show a greater decrease in current when the peak potential is reached and the concentration at the interface of the electrode is low, this is a diffusion limited reaction and can be described by equations [59]. The usual square shape of the graphs can also be an indication of charge build-up during the applied voltages, this is an indication of some unwanted capacitance. The figure also shows some reversibility issues surrounding the small shifting in oxidation peaks. Some of the shifting peak potentials can be a consequence of the electrodes not being exactly the same. There could be some variation in the fabrication method, although the same basic materials and protocols were used for this batch of electrodes. Another possibility could be the existence of multiple layers, which may cause an extra capacitance resulting in different oxidation peaks. the absence of clear reduction peaks is also an indicator of a partly irreversible electron transfer. Further experiments also showed a slight decrease in current after each cycle, this can mean that the PEDOT layer is getting more oxidised and insulated over time. This oxidation may be one of the problems of the actuator design during polymerization. Some of the literature studies use some extreme measures to counteract this problem. Some of the studies

report on using distilled pyrrole, degassed with N_2 gas and polymerised under freezing temperatures of -25 degrees Celsius [16]. This project only used the degassing to remove the oxygen from the polymerization solution. Gold electrodes were also used to check for differences.
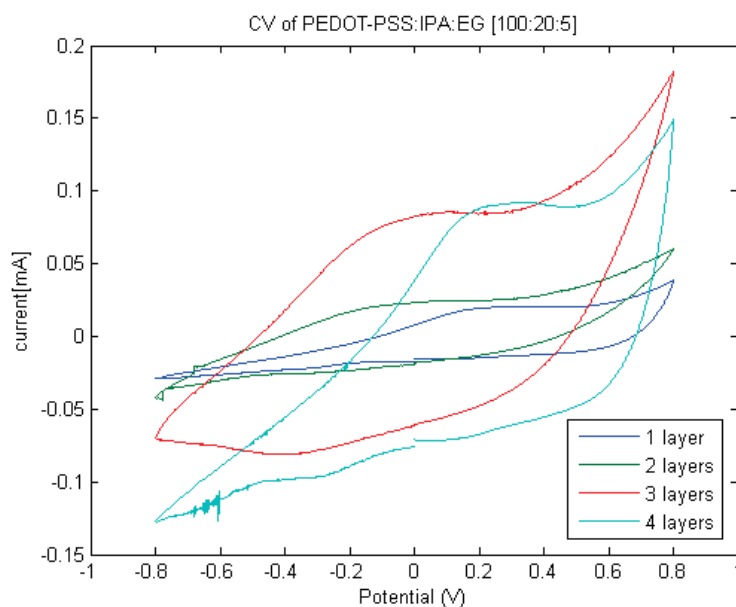

Figure 2.7: Cyclic voltametry of different number of PEDOT layers with a NaDBS electrolyte. The increasing current for multiple layers is clearly visible. Characteristics of the electrochemical system are described based on the the absence of a clear reduction peak, the flattened oxidation peak and the squared figure the different CV measurements

2.2.2. DEPOSITION OF POLYPYRROLE AND INFLUENCES ON MORPHOLOGY

Figure 2.8 shows a SEM comparison between a gold and PEDOT surface of a commercial electrode. The black part on the left image is a thin layer of PPy made in pyrrole and NaCl, the lower white part is plastic from Dropsens electrode holder. The right image is the gold surface of the Dropsens electrode . It can be clearly seen that the surface of the PPy layer exhibits a spherical morphology that is not copied from the granular surface of the gold electrode. There is however still a chance of the granular gold surface allowing for more nucleation sides for the polymerization of PPy. The effect of dopants, electrode material and current densities will be further discussed, this will later show the same spherical roughness for PPy doped with LiTFSI on thick layers of PEDOT.
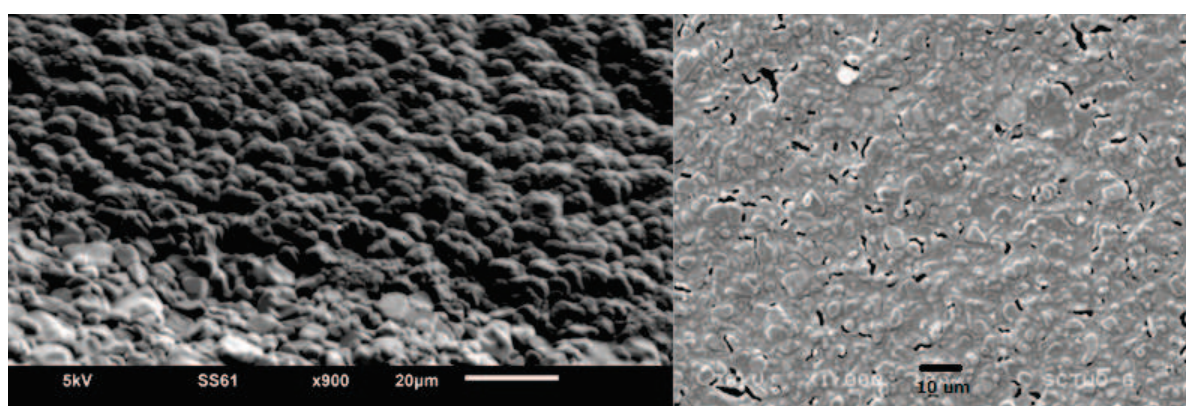

Figure 2.8: PEDOT (left) and gold (right, Dropsens.com) surface morphology, the spherical PEDOT structure is not the direct result of the granular morphology of the gold electrode surface

Using commercial electrodes provides a good understanding of the polymerization process when looked at in a scanning electron microscope (SEM). The polymerization process has many different variables such as: roughness, the material of the electrodes, the current and voltage settings, the dopant solution, polymerization time and all the concentrations of the monomer and dopant solution. By looking at these variables through the SEM, one can see the change in morphology when certain parameters are changed. By using commercial electrodes during the polymerization process these different properties can remain as constants. This will ensure that new measurements only show the response which was caused by deliberate changes in the experimental setup or by changed variables. Figure 2.9 shows the PPy layer on an gold (a) and PEDOT (b) electrodes. The image shows the different layer thicknesses and the roughness of the spherical surface of the samples. The roughness of the PEDOT sample is in the order of 1 micrometer, the thicker layer of the PPy on the gold electrode has a larger roughness in the order of 10 um. Multiple variables are different for the 2 samples, this can explain the differences. The polymerization current of the gold sample was larger because of the higher conductivity of gold, this will most likely be the reason of the thicker layers with a larger roughness. Higher current densities will form more nucleation sides for the PPy to form. this is shown in the next section.
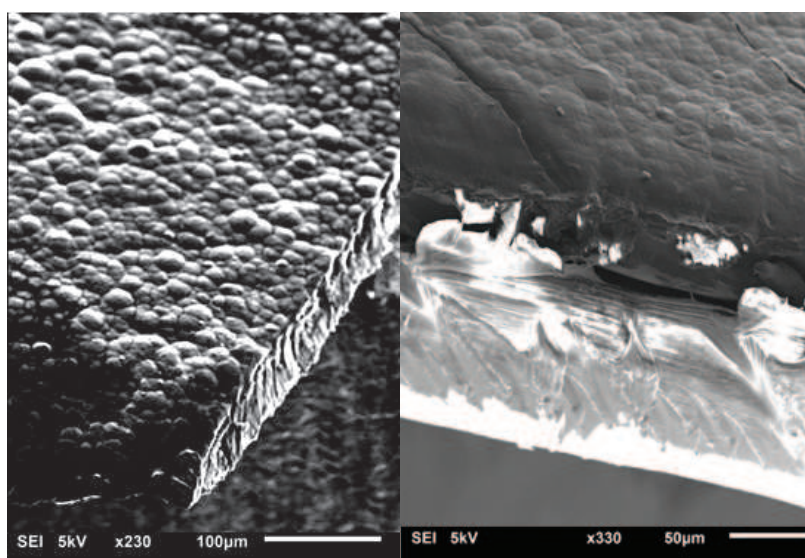

(a) A single layer of PPy, initially made on a gold electrode. (b) A Layer of PPy on top of a PEDOT-TOPAS substrate

Figure 2.9: PPY on commercial gold and PEDOT electrode. The PPy on gold shows a rougher and more spherical surface. The PPy on PEDOT (that was made with lower current densities) shows a more uniform but thinner layer

One of the variables of the electropolymerization process is the time. The polymerization time is expected to be only related to the thickness of the material. There are however some changes at the early stages of polymerisation. A normal example of polymerization with a fixed voltage is shown in figure 2.10a. Part 1 is the beginning of the nucleation of polymer chains on the surface of the electrode. At the top current the surface is covered with enough nucleation point to have the maximum polymerization speed. As the surface becomes more saturated with polymers the less conducting polymer will act as the electrode layer, the continued polymerization of this less conducting polymer will result in a declining polymerization speed (part 2). As the polymerization continues the conductivity of the polymer layer will decline until a steady state is reach (part 3) this part can consist of a slow polymerization current and the parasitic currents such as noise and unwanted current due to for instance contamination. Most of the material on thick layers of PPy were deposited in the steady state current, some of these experiments were continued for up to 20 hours.

The voltage and current will affect the morphology of PPy on different levels. There is a direct relation between the current and voltage, a set voltage is the preferred methods, it will create a specific current that is dependant on the electrochemical setup and the stage of polymerization. A set current density will change the voltage to allow for a specific deposition of material, this can result in a voltage that can over-oxidise the

(b) High local current densities
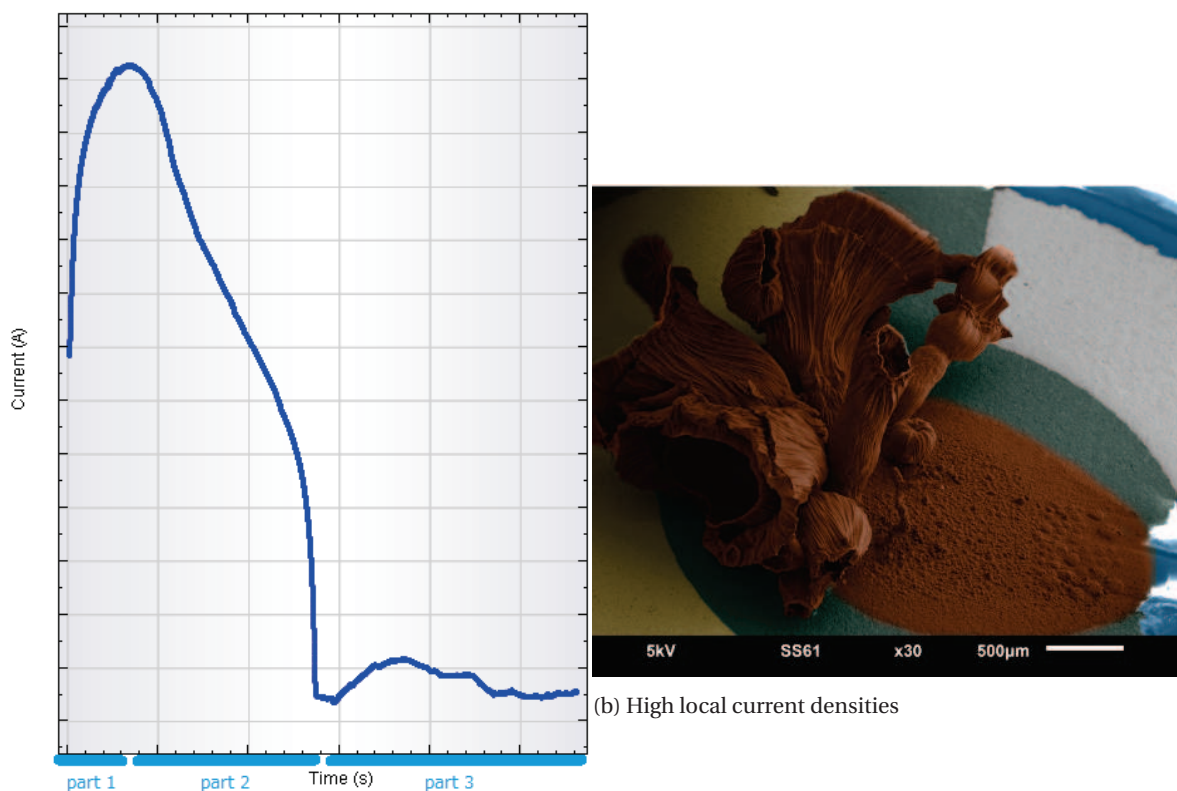
(a) A normal current plot of polymerization, divided into 3 parts, typical timescales of these features are around 1000 seconds.

Figure 2.10: The results of a polymerization without normal current densities in figure a. An example of a normal polymerization current curve in figure b, including initial rise in current (part 1), the decrease (part 2) and steadying current (part 3).

sample. The current density of the polymerization would ideally be uniformly divided over the surface of the electrode. Figure 2.10b shows an example of non-ideal locally high current densities. This specific example had a short circuit. The short circuit was the result of high local current densities, this caused local deposition of PPY that connected the 2 electrodes. Other tests show that high local current densities can form a problem. The high current densities will have a higher polymerisation rate and have an irregular shape.

The concentration and the type of dopant can also affect the morphology of the polypyrrole. These concentrations are attempted to be fixed at the literature traditional values and the effect of the 2 different dopant was studied. One of the visible changes of using LiTFSI over NaDBS is the more erratic spheres on the surface of the polypyrrole layer doped with LiTFSI, as can be seen figure 2.11. Polypyrrole (PPY) was electrochemically polymerized on top of thick treated PEDOT electrode. The base layer is a commercial sheet of TOPAS and the difference between the 2 layers is the Dopant used during polymerization. Figure 2.11a shows PPy doped with LiTFSI, there is a highly irregular morphology of small spheres. Later experiments showed these spheres to be partially hollow. Figure 2.11b shows PPy doped with NaDBS, the layer has a uniform thickness and the roughness is small compared to the other dopant. 2 explanation can be given for the change in morphology. The polymerization current showed a little higher current for the LiTFSI dopant. Another explanation can be found in the structure of the dopants. TFSI has a maximum 6 bonds between 2 atoms, DBS 30. This long chain can be the reason of a more restricted and uniform formation of PPy chains.

One of the initial problems with the polymerization process were the low polymerization rates. As predicted the distance between the working and counter electrode did not show an improvement. For better reproducible results a bigger aluminium counter electrode was therefore used instead of the previous counter electrode from the commercial gold electrode.The real improvement for the polymerization rate was accomplished when the electrical resistance of the electrode was decreased. This was done by repeating the spin
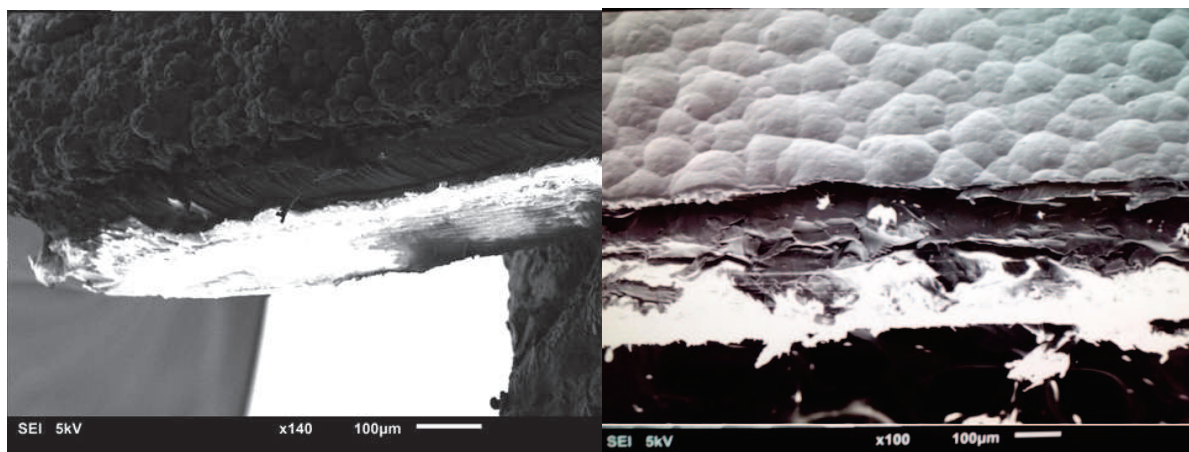
(a) PPy doped with LiTFSI on TOPAS base and PEDOT elec-trode

(b) PPy doped with NaDBS on TOPAS base and PEDOT electrode

Figure 2.11: Morphology differences of PPy layers with different dopants. The LiTFSI dopant shows a porous and rough surface, the NaDBS shows a less roughness

coating after the previous layer was dry. Because of the stacking layers that showed some adhesion problems to the substrate, extra effort was put into discovering the best procedure for the spin coating and drying of each layer. The multi layered procedure was tested for 2 to 10 layers of PEDOT. Figure 2.12 shows how the polymerization was improved with each added layer of PEDOT. The left 2.12a shows the polymerization of PPy doped with LiTFSI, the right 2.12b shows the process for PPy doped with NaDBS. The results show a smoother and lower polymerization current for NaDBS. The two figures show the increase in conductivity of the thin layer. To measure the real conductivity of the bulk material of PEDOT, the thickness of the PEDOT layer (measured by for instance a white light interferometer) and the measured sheet resistance (ohms per sq) can be used to calculate the conductivity (S per cm) which can be as high as 1418 S per cm [2]. This is almost 300 times lower than the conductivity of gold (410.000 S per cm), this means the PEDOT will need a thicker layer in order to have a comparable electrical resistance.
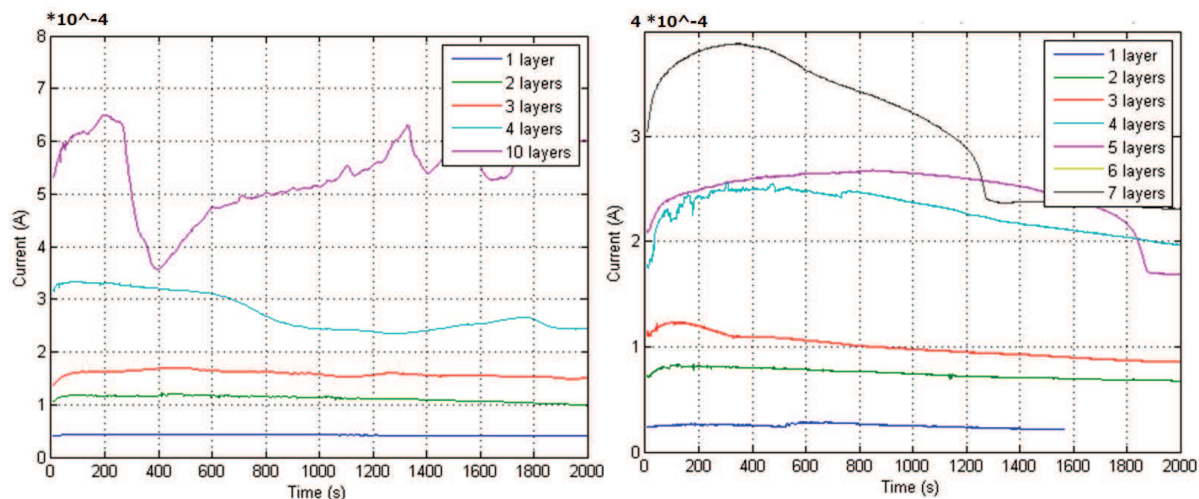
(a) Polymerization of PPy-TFSI for multiple layers

(b) Polymerization of PPy-DBS for multiple layers

Figure 2.12: PPY on TOPAS-PEDOT electrode at 0.62V using different dopants. the TFSI plot shows higher and more irregular currents, which can result in rougher surfaces showed earlier

The NaDBS Dopant was used for further development of the design. Thick layers of treated PEDOT were used for the polymerization at a low and fixed voltage. These parameter were choose to ensure uniform layers

with the most reproducible and steady results.

FARADAY'S LAWS OF ELECTROLYSIS
Faraday's laws of electrolysis in equation 2.2 is used to calculate the total PPy mass during the electropoly-merization. The reaction at which the polymerization takes place is a oxidation reaction that uses a specific amount of electrons for oxidising monomers. a total of 2 electrons are used for each monomer that is incorporated into the chain of the polymer. The currents measured by the potentiostat during polymerization can be used to calculate the total amount of electrons that have passed through the system.

$$m = \left(\frac{Q}{F}\right) * \left(\frac{M}{z}\right) \tag{2.2}$$

Q = charge = Integral (current over time)
F = Faraday constant = 96485
M = molar mass Ppy
Z = electrons used for polymerization of a single pyrrole monomer = 2 electrons
Solving the equation for M = mass = (charge / 96485)*(67.09/2)

Figures 2.13 shows the mass accumulation during the polymerization. The mass axis is logarithmic plotted. The left image shows the mass built-up for PPy doped with NaDBS, the right image shows the mass built-up for PPy doped with LiTFSI. Mass calculations can be used for multiple purposes. Usually the mass of a layer can be used to calculate the thickness. Since the PPy layer has some porous elements and a high roughness this would not show reliable results.

In commercial fabrication of PPy layers the mass calculation can be used for resupplying the monomer solution, the PPy that is formed during the process must be replaced to keep a reliable concentration of pyrrole monomer.
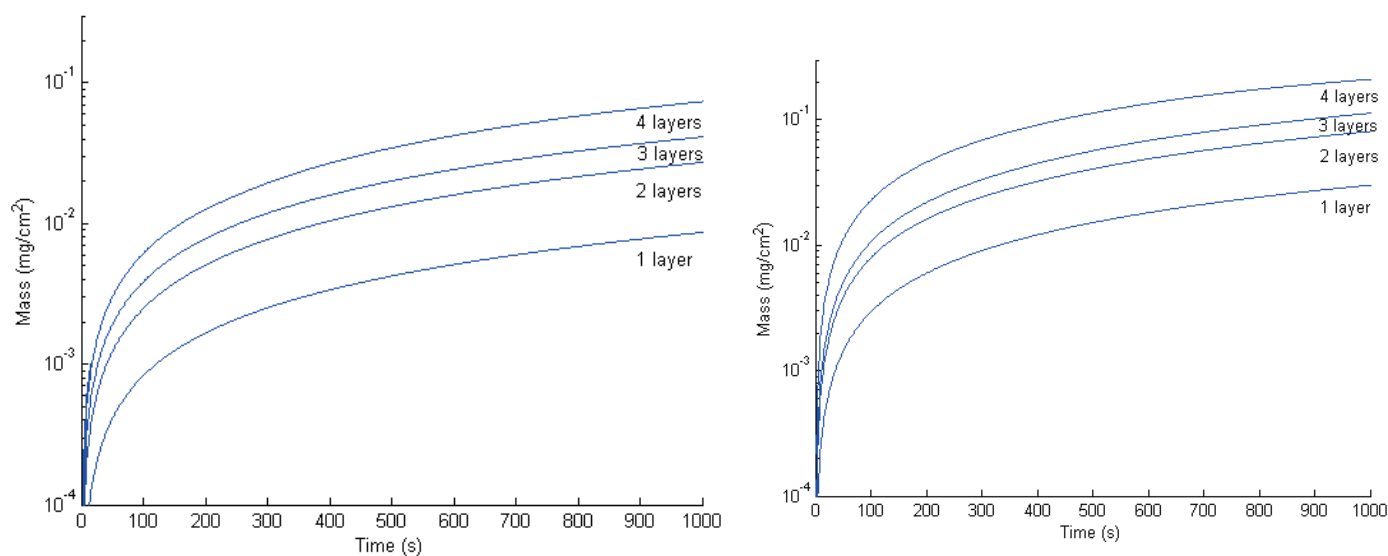
(a) mass accumulation of PPy-DBS for different number of layers of PE-DOT

(b) Mass accumulation of PPy-LiTFSI for different number of layers of PEDOT

Figure 2.13: Mass accumulation of PPy on TOPAS-PEDOT electrode

The mass accumulation graphs show the similarities of the polymerization process, the LiTFSI dopant and more layers will produce a thicker layer in the same time. There is however a comparable mass accumulation increase after the first 300 second.

2.2.3. ACTUATION
The actuation was predicted to be clearly visible without the need for equipment such as a microscope. A microscope was used to look for smaller actuation, instead of using a PEDOT electrode, a gold electrode was used to look if this would change the actuation that was not yet discovered. Figure 2.14 and 2.14 shows the

first and second test cycle of actuation of a TOPAS layer. TOPAS with a 40 nm gold electrode and a thick layer of PPy-NaDBS were used. The expected displacements of the actuator was estimated to be in the order of 2 larger then depicted here, see section 2.1.1. The displacements show a pattern in which there seems to be movement after a change in the applied voltage. Since the measurements are small and irregular it is hard to make a conclusion about the micro actuation of the actuator. Further actuation attempts showed less actuation. The measured actuation could include a drifting factor caused by vibrations, measurement errors or drifting of the sample holder. Further study with higher resolution and more vibration dampening equipment could possibly give more conclusive results.

Figure 2.14: Actuation attempts at 0.7 V
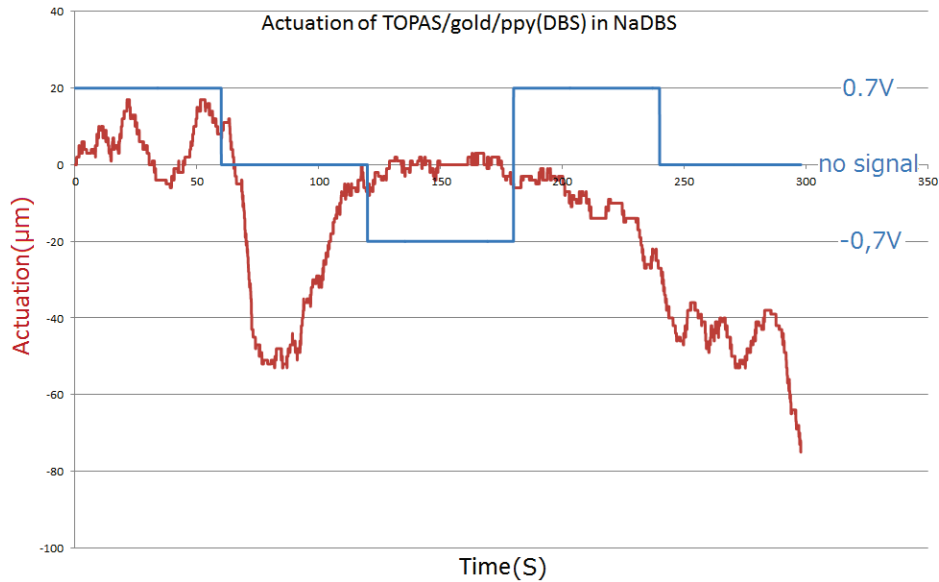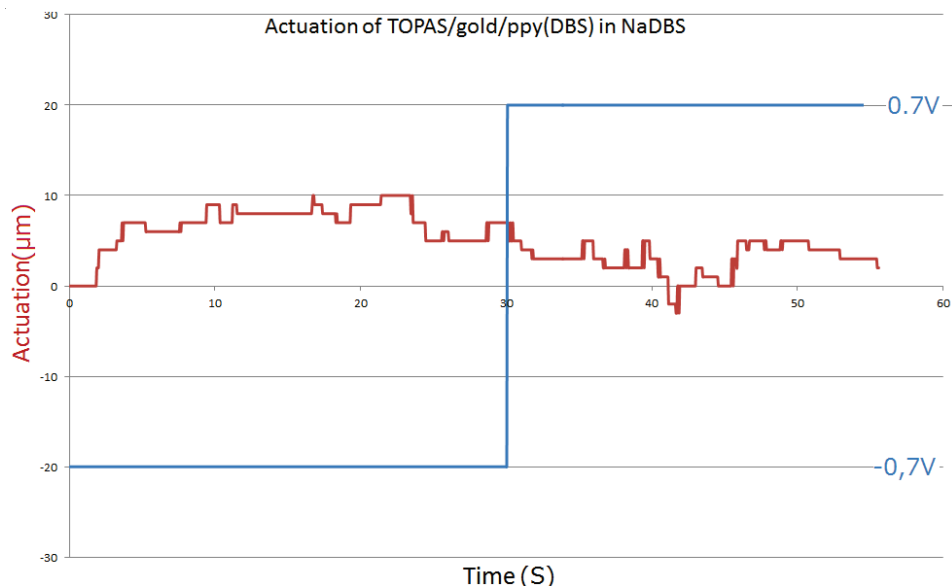

Figure 2.15: Actuation attempts at 0.7 V

PROPOSED MICROFLUIDIC VALVE SYSTEM

The goal of the conducting polymer actuator is to be implemented into a microfluidic system. A simple copy of a small beam system, see part C as a modular component in a system is pictured in figure 2.16. Because the beam is added to the system an extra layer has to be implemented to separate the working fluid and

the electrolyte that is needed for the actuation. This layer can be similar to the normal PDMS layers in Quake valves. The valve will close when the PPy side is expanded, see part A and C. The addition of multiple actuators could form a peristaltic pump
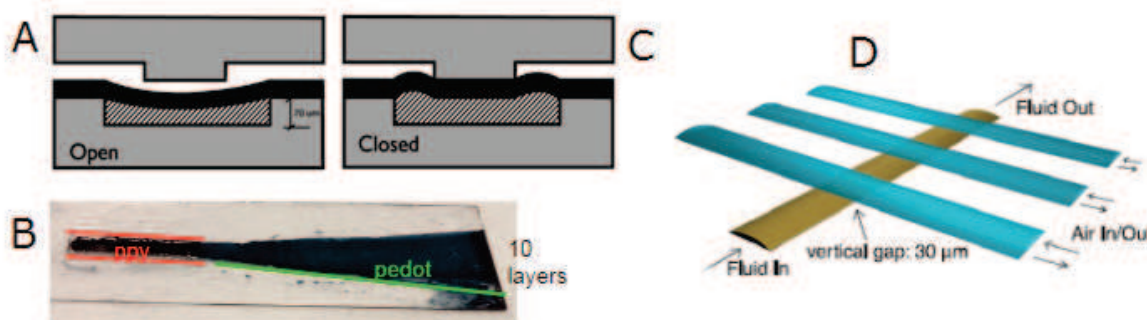

Figure 2.16: Concept of making a peristaltic pump using multiple conducting polymer micro valves

One of the main advantages of the all polymer actuator is the easy fabrication method that can easily be scaled to high volumes. An improvement to the implementation of a conducting polymer micro valve can be made if the whole microfluidic system is made without modular actuators, see figure 2.17. Like mentioned before, this would mean that all the active and electrical components are already on 1 layer of TOPAS. This layer can be compared to the PDMS layer in a quake valve. Patterning can make this possible by making patterns in the electrode that covers the whole layer of TOPAS. These patterns can be electropolymerized with expanding conducting polymers on specific identified spots. The remaining patterns can form the electrical lines that supply electrical signal for actuation. Figure 2.16 also shows a system of multiple micro valves that form a peristaltic pump which can also be achieved by patterning of PEDOT electrodes.
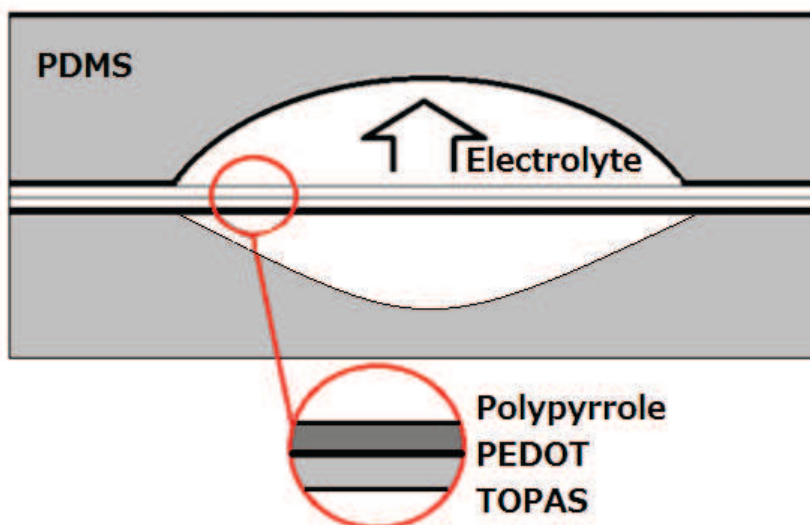

Figure 2.17: replacement for Quake valve

Another advantage of using patterning is the opportunity to implement higher resolution methods to make the systems smaller. Future techniques can also include soft or hot embossing, this is already done on thin films of PEDOT [55].

2.3. CONCLUSION AND OUTLOOK

2.3.1. CONCLUSION

Designing an all polymer microfluidic valve with a conducting polymer actuator has a lot of advantages over traditional Quake valves. Because there are many disciplines involved in this subject, there is also a wide variety of problems that need to be solved in order to get a working prototype. This report focuses at the most basic problems that arise during the fabrication of the layers of polymers.

The first subject that was addressed, was the different morphology of the material when using different electrode materials. This can be ascribed to the speed at which the polymerization occurs. This speed is measured in current per area. In the experiments it was found that the polymerization speed is related to the electrical resistance of the working electrode. This became clear when looking at the short circuit of figure 2.10b . The short circuited parts of the material received a high current which allowed the polymerization to spin out of control. Opposite to this high current was the absence of polymerization when working with a PEDOT electrode. The low electrical conductive properties of PEDOT-PSS caused a resistance limited electropolymerization reaction. This problem was solved by increasing the conductivity of the material in 3 specific ways. The first was the addition of isopropanol to get a better wettability and uniform layer of the samples. The second was a treatment of ethylene glycol that rearranges the PEDOT orientation and increased the conductivity. The third was the addition of multiple stacked layers of PEDOT-PSS, this increased the thickness and thus the overall conductivity of the electrode.

The second and third subjects were the problems around the PEDOT electrode. PDMS and TOPAS. The adhesion of PEDOT to PDMS and TOPAS was investigated by looking at the composition of PEDOT and its additives, the pre-treatment with plasma,cleaning methods, the spin coating speeds, drying times and temperatures and finally the removal of the material from the base layer of PP or glass.

The fourth subject was the experimental method to fabricate and actuate the PPy actuators. After looking at the adhesion and the conductivity of the PEDOT electrodes, the layers of PPy was fabricated on top of the PEDOT covered TOPAS foils. To actuate the material some variables in the fabrication and actuation process was studied. Two different dopants for PPy were used, different electrolyte solutions were tested for the actuation, handling methods were tested to minimise the oxidation of the samples and finally the PEDOT was replaced by gold to make a comparison.

The fifth subject was the opportunities that arise with all polymer microfluidic valves. The main advantages of the new system were the possibilities for low cost mass production of thin films of TOPAS with patterned PEDOT electrodes and locally electropolymerized active parts of PPy. These films can be used in microfluidic systems to replace the pneumatic Quake valve systems. Multiple methods for the patterning of PEDOT electrodes were discussed. The first group of methods used some sort of mask to only deposit PEDOT to the parts of the system that would be used for the conductive properties of the PEDOT coating. The second method was the fabrication of non conducting traces using embossing of a fully PEDOT covered system. This Embossing method had the advantage of the easy fabrication of PEDOT covered foils and highly accurate and fast embossing.

2.3.2. OUTLOOK

The realisation of a working all polymer microfluidic valve is an opportunity for a wide variety of research fields. In the field of chemical engineering a lot of research is done on the chemical processes that influence the actuation speed of the active polymers layers. Electrolytes solutions, Dopants, expanding conducting polymers, electrodes, they can all be studied with varied concentrations and different materials. In the field of mechanical engineering several aspects of the dynamic properties can be studied. Possibilities include the displacement and elongations of thin foils during the actuation of the conducting polymer. The material itself shows unique properties during expansion of the material in which the dimensions increase but the young's modulus do not increase but decrease. This can be used to design valves under pre-stress that can click in an open and a closed position. Patterning of PEDOT on TOPAS substrates is already investigated using soft embossing but can be further researched to include thicker multiple layers of PEDOT or thin layers of gold. One of the ways a conducting polymer valve could be used is when multiple rows of valves work together to

create a peristaltic pump. The patterning opportunities of an all polymer design are a great combination in the easy fabrication of complex systems that include multiple valves, pumps and even sensors that work with polymerization on the PEDOT electrodes. The idea of using the easy but versatile fabrication and low power requirements offers a lot of possibilities for fabricating disposable lab on chip devices that are portable and affordable using microfluidic channels, valves, pumps and even sensors.

3

REFLECTION

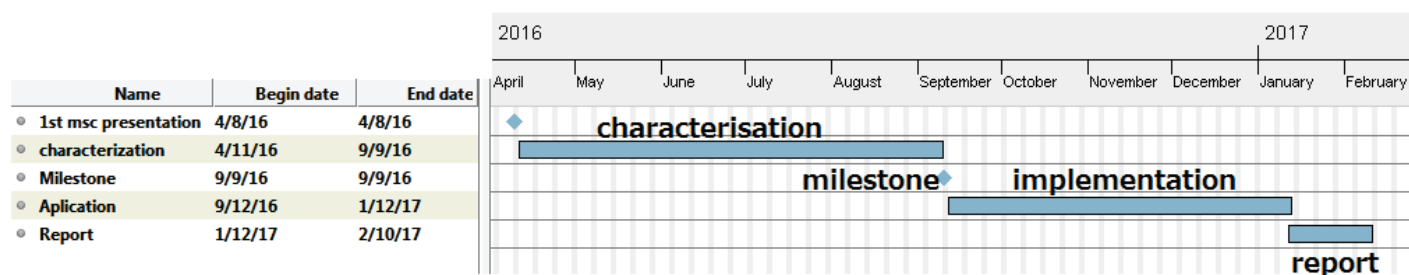## 3.1. TIMELINE
3.1.1. INITIAL TIMELINE

Figure 3.1: initial planning

The initial timeline presented at the first master presentation (see figure 3.1) estimated the time planning for this project. The initial planning contains 2 parts, divided by a milestone in which an evaluation took place.

The first 4 month (and a month summer vacation) was reserved for the characterisation of the material. This characterisation would include the polymerization of PPy, Spin Coating of the PEDOT electrode material and fabricating the PDMS/TOPAS base layer. The last part of the characterisation was supposed to be used for the investigation into the properties of the expansion of the material.

The milestone in September would include the evaluation of the characterisation. This evaluation would determine the content of the implementation period of the project. A successful characterisation would result in the implementation of a microfluidic system that could show a working prototype with the possibility of performing experiments on the properties of the actuator.

The second part that was planned to last for 3 months (and two weeks vacation at the end of the year). The implementation was planned to include the fabrication of a microfluidic channel in which the active PPy layer could close, or at least to some degree control, a flow inside a microfluidic channel. The characterisation of this microfluidic system would be investigated. The working principle of the actuator was supposed to be the same method of applying PEDOT as the electrode to a base layer followed by the electropolymerization of PPy. The actuator was, in contrast to what is reported in the final procedures, planned to be cut into a small beam and inserted into a microfluidic system. This was going to make the system modular, but also introduced manual installation steps of inserting the actuator inside the system. The planning for unexpected difficulties included design adjustments. Concessions in the project could be made if there were too much adjustments needed. Ways of dealing with unexpected difficulties included the extension of the project or investigating if there was useful subjects that could offer some new understandings.
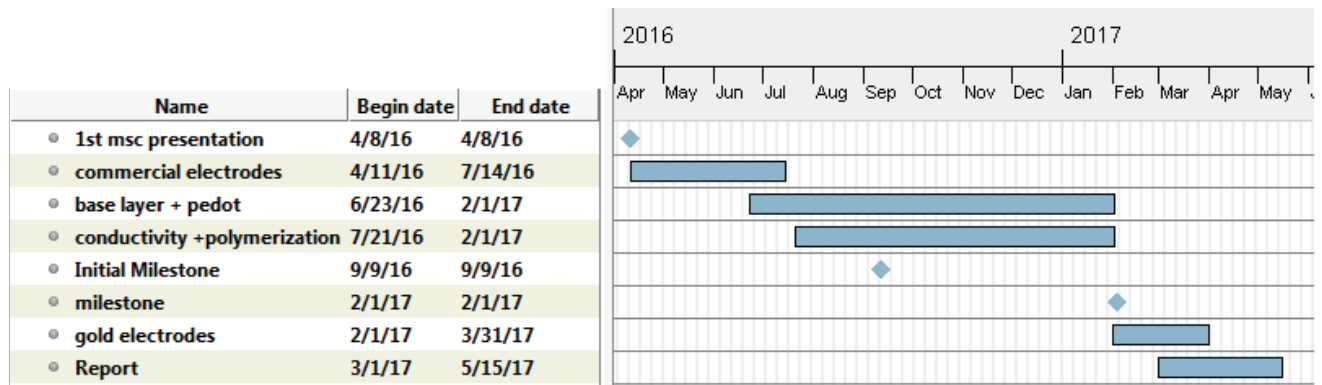
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3.1.2. FINAL TIMELINE

Figure 3.2: final planning

The final timeline (see figure 3.2) is divided into more parts than the initial planning, the initial milestone is still present. There is not a separate actuation part in the final timeline, instead the actuation was tested after each design change.

This chapter will further discuss the line of thought regarding the scientific method of developing the conducting polymer microfluidic valve. Each part of the project was performed with the following method in mind:

1. The first step is to analyse a part of the design and to make a problem formulation.

2. By researching literature and doing initial tests possible solutions are formulated.

3. The solution is tested with experiments.

4. These experiments are then evaluated and new research questions will be formulated if needed.

COMMERCIAL ELECTRODES
During the first section of the project commercial electrodes were used to look at the polymerization deposition in a more controlled environment of electrodes with known properties and dimensions.
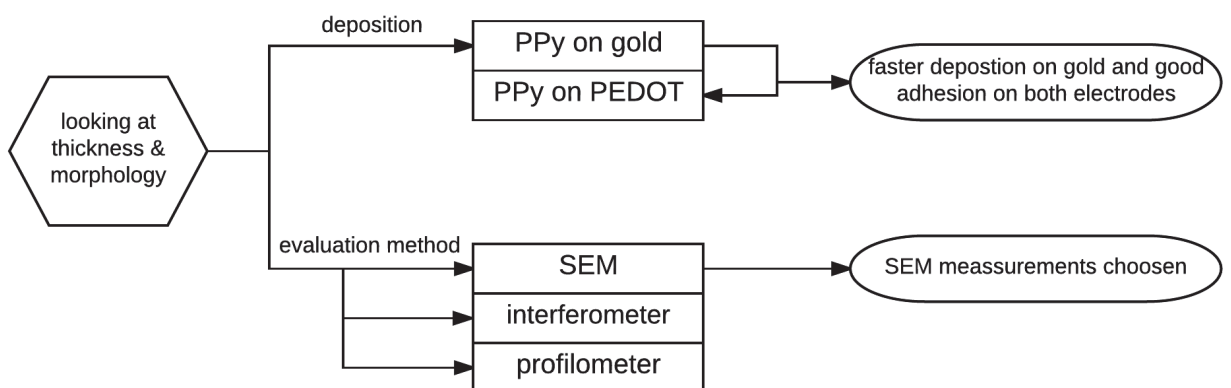

Figure 3.3: Methodology of commercial electrode experiments

Figure 3.3 shows the steps for looking at the basic properties of polymerization of PPy on standard screen printed gold and PEDOT electrodes. The goal of this part of the project was to get familiar with the procedures

used in literature and to get a feeling for the results of varying the parameters such as voltage, concentrations and electrodes. The first steps included the deposition of Polypyrrole on gold, these experiments were performed with concentration and voltages commonly used in literature. After successfully depositing and evaluating the PPy layer on gold, a PEDOT electrode was used for the polymerization of PPy. The difference between the 2 electrodes was clearly visible, see figure 2.9 This part of the project showed insight into the deposition process of polypyrrole, together with the possibilities of the different lab equipment instruments, in particular the SEM. This step was a good use of effort for learning the different techniques and producing some nice SEM images.

BASE LAYER AND PEDOT ELECTRODE
The second part of the project was focused on making a base layer of PDMS and later TOPAS. This layer was then covered with a PEDOT layer as an electrode.
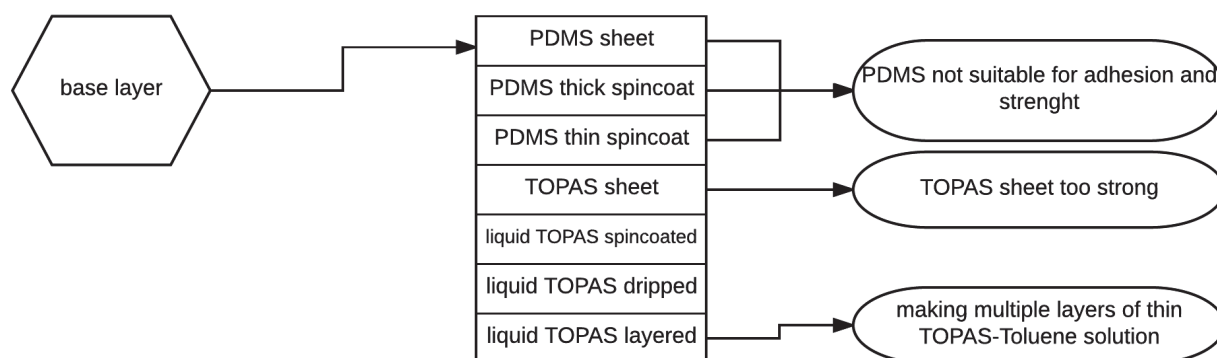

Figure 3.4: Design of flexible base layer

Figure 3.4 shows the steps for looking at the design of the flexible base layer. The problem formulation is the requirement of making a flexible base layer with a customizable thickness. This layer needed to have sufficient adhesion with PEDOT and fabrication had to be possible with the lab equipment that was available. Different sheets of PDMS and TOPAS were made and PEDOT adhesion and layer fabrication was tested. The layer that was easiest to fabricate was by dissolving TOPAS granules in a Toluene solution and covering a glass or PP surface for multiple times. Spin coating multiple layers was used for specific experiments that required thinner layers, dripping the TOPAS-Toluene was used to quickly produce big sheets of TOPAS. a lot of new possibilities presented itself after the discovery of the method of making custom layers of TOPAS. If there was more time the roughness of TOPAS could have been studied. This had a big effect on the adhesion of PEDOT to PDMS.
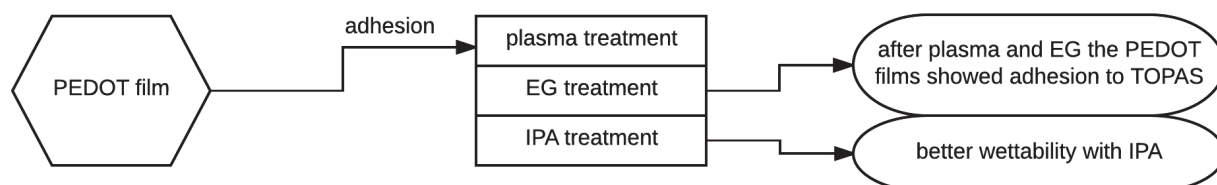

Figure 3.5: PEDOT film

Figure 3.5 shows the steps taken looking at the design of the PEDOT electrode layer. The first design stage was targeted towards the adhesion properties of the PEDOT films. Plasma treatment of the TOPAS films was needed for the liquid PEDOT-PSS solution to adhere to the TOPAS surface. The EG treatment did not greatly

influence the adhesion of the liquid PEDOT-PSS, but made the dried film of PEDOT-PSS-EG more water resistant. This problem initially made spin coated PEDOT electrodes dissolve during and before polymerisation. The choice of using a PEDOT-PSS-EG solution instead of an EG after-treatment was made after experiments showed no significant differences. IPA was added to the PEDOT-PSS-EG mixture to get a better wettability for the spin coating. This resulted in more uniform PEDOT films. Finally the process of evaporating the liquids in the PEDOT-PSS-EG-IPA solutions was improved by longer drying times and higher temperatures that would still allow the PEDOT to be conductive and the TOPAS to not reach the glass transition temperature.

This part of the project introduced the first hard part of the research. The adhesion of an electrode material on a flexible polymer substrate was a hard process optimise. a lot of effort went into the process of ultimately finding a way to make specific layer thicknesses of a polymer material that showed good adhesion and other characteristics like strength and chemical resistance. The PEDOT film adhesion process was also hard because of all the process steps that needed to be optimised for the fabrication.

MILESTONE
At the planned milestone in February the progress of the project was evaluated. The characterisation of the material was planned to be finished at this point, however the actual progression appeared to take more time than initially expected. The main reasons for this delay were difficulties with the replication of the literature studies and with using PEDOT as an electrode for polymerization of thick layers (in a water solution). It was decided to continue with the basics of the design of the actuator, and mainly focus on the next list of unexpected problems:

- The base layer with specific thickness was more difficult to fabricate than expected.

- Adhesion of PEDOT to a substrate was a bigger problem than was initially planned.

- PEDOT conductivity problems during polymerization.

- Replication of actuation experiments didn't yield results.

The goals of the project were adjusted for the successful actuation of an all polymer actuator- after all the basic initial problems were solved.

CONDUCTIVITY PEDOT
The next part was the investigation into why single layer PEDOT electrodes often don't work for making thick layers of PPy, this also includes the adhesion problems.
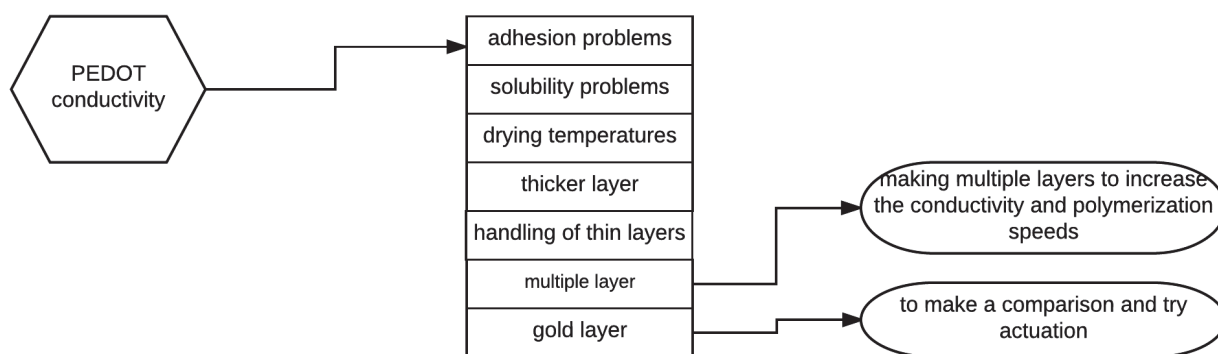
Figure 3.6: PEDOT investigation

Figure 3.6 shows the steps that were taken for looking at the conductivity improvements of the PEDOT film. At first the adhesion, solubility, drying temperatures, handling and thicknesses variations were tested for the improvement of the conductivity of the PEDOT layer. The best variables were then used to make multiple layers, since the best 1 layer system didn't allow for a good polymerization electrode. After making thick layers of PEDOT the polymerization of thick layers of PPy was not a problem. The actuation was however not

comparable to literature.

SECOND MILESTONE

During the second milestone the decision was made to replace the PEDOT electrodes with gold electrodes. This decision was made because the gold allowed a faster approach in making actuators that were possibly better than PEDOT and more similar to available literature studies. The next goal was to get an actuator with some kind of actuation comparable to literature.

ACTUATION

During the whole project actuation attempts were performed. Figure 3.7 shows the different experiments that were performed to improve the chances of making the actuator work. This includes the use of gold electrodes in part 4. For the reduction of oxidation N_2 gas was use to remove the oxygen in the solutions, the sample pieces were kept in a liquid at all times and the removal from the base substrate was improved by using glass or removing the substrate before further processing.

Figure 3.7: Actuation

3.2. CONTRIBUTIONS
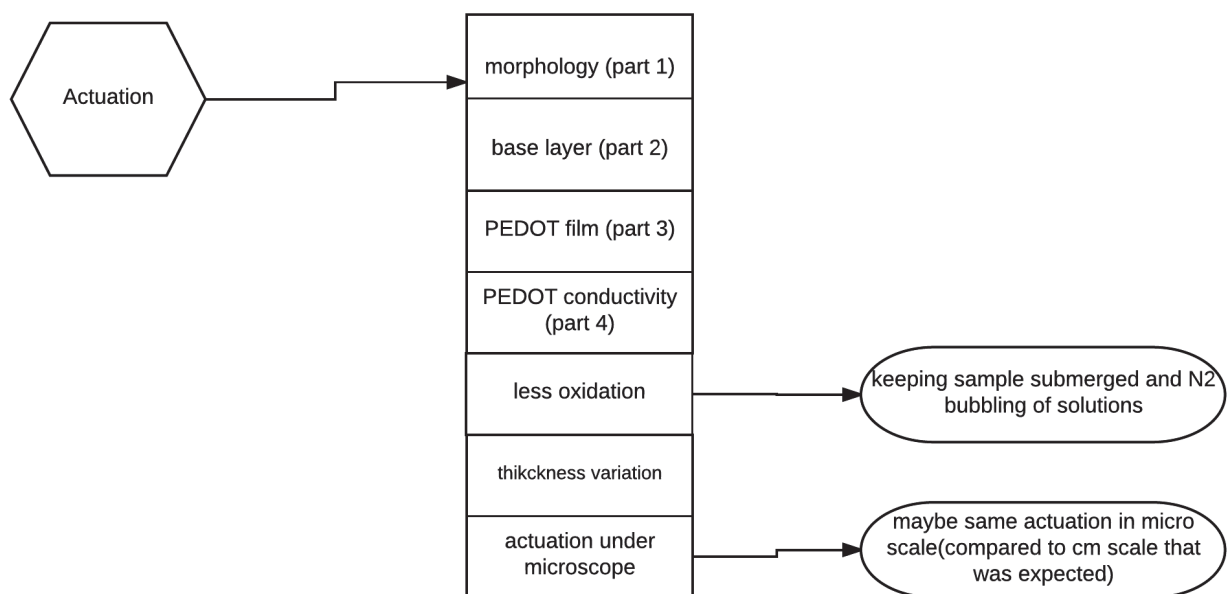
This section will give a brief overview of the the contributions regarding the project. The project supervision was a collaboration between Assistant professors Murali Ghatkesar and Luigi Sasso. Luigi Sasso is an expert in the field of polymers and therefore advised on this subject during the project. Murali Ghatkesar is an expert in the field of microfluidic systems and advised on this particular part of the project. The project was performed at the Micro and Nano Engineering (MNE) group which is led by professor Urs Staufer. The MNE group is part of the Precision and Microsystems Section within the faculty of Mechanical Engineering. During multiple meetings and presentations the experts and students of this group gave a lot of helpful contributions regarding the project in the form of new ideas, how to solve certain problems and how to improve presentations.

Different people of the MNE department played a role in this project. Bas Smit used his project about polymers micro structures to help with the beginning of the project by showing experimental setups and giving his ideas on the project. The research of Chi-tung Chang about polymers sensors was used to make a start with experimenting regarding the best spin coating variables of PEDOT-PSS-IPA. Pieter Kapelaan also had a project in which polymers were used. The TOPAS and PEDOT protocols of this projects were used for his project. Postdoctoral researcher Dr. Paola Fanzio played an important role in choosing TOPAS as a replacement for PDMS. When the PDMS appeared to be a bad combination with PEDOT electrodes, she was consulted in the discussion about using TOPAS. Her research used different TOPAS samples. Some of her materials were initially used for testing the feasibility of using a flexible base layer of TOPAS. During the project I have become well acquainted with the MNE department and all the labs of this department. Because of this knowledge I was able to help other students with their research projects. Various students were helped with the process of acquiring better SEM pictures for example. I also introduced the plasma etcher, the spin coater and the clean room procedures to various students. Lastly I have given several presentations during an open day. During this day the MNE part of the PME master of mechanical engineering was introduced to primary school students and their parents.

Various people outside the MNE department were consulted regarding the project. Jörg Strack (Market Development of TOPAS Advanced Polymers GmbH) was contacted for information about the possibilities of spin coating TOPAS. After correspondence about the absence of commercial availability of TOPAS in a solvent, possibilities of making a TOPAS liquid solution were supplied. This resulted in the use of toluene as a solvent for TOPAS. Also TOPAS granules were supplied for the project by TOPAS Advanced Polymers GmbH. Mechatronic System Design (MSD) Msc student Raoul Timmerman showed his setup in which a commercial IPMC actuator was tested. This setup and possible applications of this setup for this project were discussed in the initial stage of this project, before the results of the actuation were investigated. Various times the project was discussed with MSD MSc student Rens van de Nolle, his ferroelectric actuator showed similarities with the actuator principles from this project. His challenges with initial small actuation displacement were the basis for this project to look at the actuation at micro-scale.

LITERATURE

The starting point of this project were the papers from Berdichevsky [1] and Lefevre [13]. Their research showed good applications of microfluidic valves from conducting polymers. One of the problems with these papers were the discontinuation of their work, their papers showed results but the polymerization method and actuation results were hard to replicate under different circumstances.

There are various research groups that have focused their attention at conducting polymer actuators.The group of Elisabeth Smela has published about conducting polymers actuators for almost 20 years. Their research include PPy microfabrication [60], modelling of PPy [61], conjugated polymer actuator reviews [62], PPy-DBS relaxation [63], ion transport[64] and a project similar to this project , in which a patterned actuator is made on a thin polymeric film [65].

4

APPENDIX

4.1. DATA

		Polymer Microvalve Based on Anisotropic Expansion of Polypyrrole	A polymeric micro actuator to be integrated into an organic material based lab on chip microsystem	Performance Quantification of Conducting Polymer Actuators for Real Applications: A Microgripping System
1				
2	type of microvalve	piston type layer	piston type layer	5 layer beam
3	working principle	anisotropic volume change of layer on protruded post	anisotropic volume change of layer	more-layer expansion bending
4	**Dimensions**[um]			
5	length	110	>100	5000
6	width	110	>100	1000
7	thickness	34	50	170
8	**Deposition**	electropolymerization	electropolymerization	sheet of conducting polymer
9	Conducting polymer[mol]	polypyrrole(0.04)	polypyrrole(0.1)	
10	Dopant[mol]	NaDBS(0.04)	NaDBS(0,1)	
11	electrode	gold	gold	
12	deposition time[hr]	4.3	0.1mA/cm2	
13	thickness layer			
14	fabrication explained?	+++	+++	*
15	**Actuation**			propylene carbonate solution for less dissipation of fluid
16	electrolyte[mol]	NaDBS(0.01)	NaDBS(0,1)	TBA PF6 0.05 M (tetrabutylammonium hexafluorophosphate)
17	voltage[V]	- 1 to 1		0 to 1
18	speed	10-15sec(12%)		10 sec
19	force			0,8 to 1mn(10-1pulse/min)
20	% expansion	32		8mm curve
21	reversable(%)	12% (34um-45um-40um-45um)		100%(bilayer)
22				
23	disadvantages	bonding au-ppy		
24		thermal depositino of ti au		
25		photolithography/cleanroom		

		Fast trilayer polypyrrole bending actuators for high speed applications	Microfabricating Conjugated Polymer Actuators	Highly Stretchable and Powerful Polypyrrole Linear Actuators	TFSI-doped polypyrrole actuator with 26% strain	Comparison of Conducting Polymer Actuators Based on Polypyrrole Doped with BF4 , PF6 , CF3SO3 , and ClO4
2	type of microvalve	5 layer beam	patterned layers			
3	working principle	more-layer expansion bending	bending through expansion			
4	**Dimensions[um]**					
5	length	10000-40000	50-300			
6	width	2000	20			
7	thickness		1,5			
8	**Deposition**	electropolymerization	electropolymerization	electro polymerization	electro polymerization	electro polymerization
9	Conducting polymer[mol]	0.06 M pyrrole	polypyrrole(0.1)			
10	Dopant[mol]	0.05 TBA−PF6	NaDBS(0,1)			CF3SO3
11	electrode	gold	gold			
12	deposition time[hr]	12hr (0.10 mA/cm2)	0.1mA/cm2			
13	thickness layer	15um				
14	fabrication explained?	+++	+++			
15	**Actuation**	propylene carbonate solution for less dissipation of fluid				
16	electrolyte[mol]	TBA−PF6, x M (tetrabutylammonium hexafluorophosphate)	NaDBS(0,1)			tetrabutylammonium trifluoromethanesulfon ate
17	voltage[V]	1v	0,5 to 0,6			
18	speed	1Hz to 10 hz(22mm - 2mm)	2sec			
19	force	0,8mn				
20	% expansion	22mm (40mm actuator)	180 degrees			
21	reversable(%)	100%(bilayer)				

```matlab
 1 -    clear
 2 -    clc
 3
 4
 5 -    h1=100*10^(-6);%PPy sources!
 6 -    h2=5*10^(-6);    %TOPAS
 7 -    E1=300*10^6;%PPY
 8 -    E2=2600*10^6;%TOPAS, 8007 TOPAS
 9 -    a1=1.02;%literature expansion of PPy
10 -    a2=1;
11
12
13
14 -    H1=1;
15 -    for h1= [25:5:70]*10^(-6)
16 -         H2=1;
17 -         for h2= [1:1:95]*10^(-6)
18
19 -         m=h1/h2;
20 -         n=E1/E2;
21
22 -         Kr=((a1-a2)/h2)*(6*m*n*(1+m))/(1+4*m*n+6*(m^2)*n+4*(m^3)*n+(m^4)*(n^2));
23 -         R(H1,H2)=1000/Kr;
24
25 -         H2=H2+1;
26 -         end
27
28 -    H1=H1+1;
29 -    end
30
31 -    contour(R,'ShowText','on')
32 -    set(gca,'Ytick',[1 5 10],'YTickLabel',[25 50 75])
33 -    % set(gca,'Xtick',[1:1:95],'XTickLabel',[5:20:95])
34 -    ylabel('Height of PPy layar (um)'), xlabel('Height of TOPAS layar (um)'), ...
35 -        title('Bending of a cantilever beam, contour is radius of curvature in mm ')
36
```

Figure 4.1: bilayer bending

```
1      %%import data
2
3 -    delimiterIn = ';';
4 -    headerlinesIn = 1;
5
6 -    S=7;%samples
7
8 -   ☐for I = 1:S %files must be labeled 1 to how many samples(no ' .txt ' )
9 -        filename = int2str(I);
10 -       A(I) = importdata(filename,delimiterIn,headerlinesIn);
11         %%calculate charge
12 -       charge(I) = trapz(A(I).data(:, 1),A(I).data(:, 3));%charge = ....
13 -       m(I)= (charge(I) / 96485)*(67.09/2);%m=mg?
14 -    end
15
16
17     % plott=''%automating what to plot
18     % for J = 1:S
19     %      plotting=['A('  int2str(J)  ').data(:, 1),A('  int2str(J)  ').data(:, 3)'];
20     %      plott=[plott ',' plotting];
21     % end
22     % plott
23
24 -    figure%'semilogy' instead of 'plot' for logaritmic plot
25 -    plot(A(1).data(:, 1),A(1).data(:, 3),A(2).data(:, 1),A(2).data(:, 3),A(3).data(:, 1
26 -    grid on
27 -    title('Amperometry of polypyrrole on top of pedot electrode with multiple layers, O
28 -    xlabel('Time (s)')
29 -    ylabel('Current (A)')
30 -    legend('1 layer','2 layers','3 layers','4 layers','5 layers','6 layers','7 layers')
31 -    axis([0 2000 inf inf])
32
33
```

Figure 4.2: charge to mass calculation

SEM IMAGES

figure 4.3 shows a layer of PPy that is electropolymerized on top of a gold commercial electrode, the thin gold electrode is coloured in gold with photoshop.
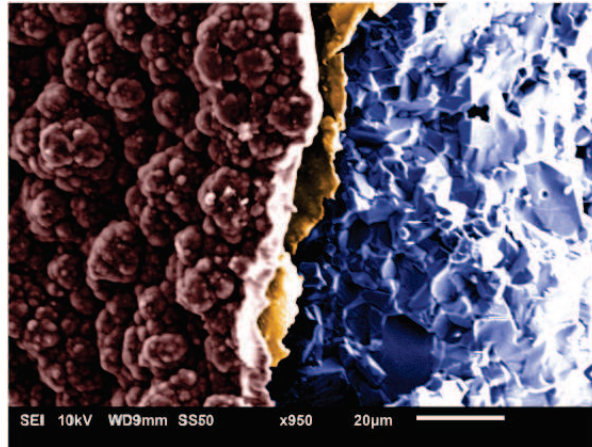
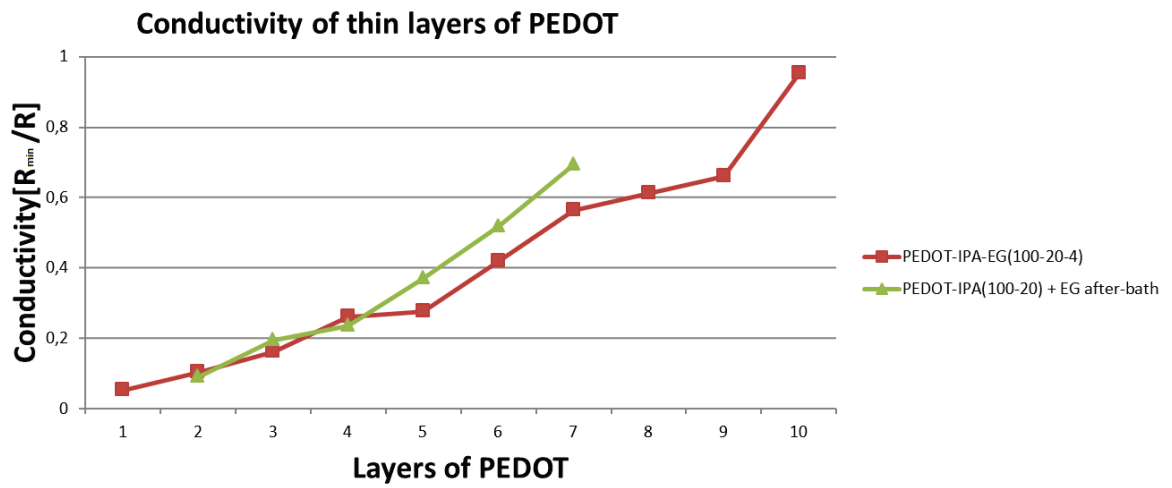Figure 4.3: polypyrrole on gold commercial electrode

Figure 4.4: effect of EG bath

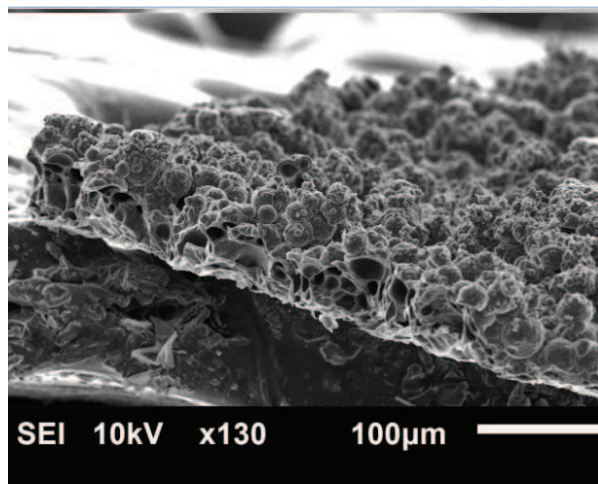Figure 4.5: Commercial PEDOT electrode system(http://www.dropsens.com)
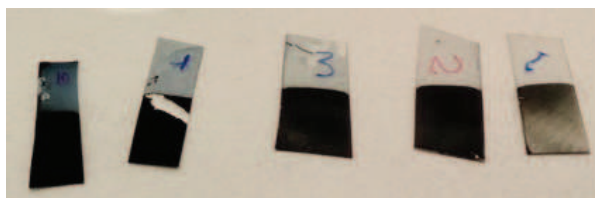
Figure 4.6: polypyrrole

Figure 4.7: PPy testing on different layers PEDOT

figure 4.5 shows the commercially available screen printed gold electrode from dropsense (DRP-P10), the working electrode consists of PEDOT (4 mm diameter), the counter electrode is made of carbon and the reference electrode is made of silver.

figure 4.6 shows a manually delaminated PPy layer that is electropolymerized on top of an electrode that consists of 10 layers of PEDOT-PSS-IPA-EG

figure 4.7 shows okt26pedotlayers testing PPy on different layers of PEDOT.

figure 4.8 shows a pattern that is made by spray coating a surface, the coating is inside the red markings, ans is made using a polypropylene(PP) mask that covers the rest of a glass microscope slide.

figure 4.9 shows the patterning using spin coating PEDOT while mask of a maskt of polypropylene(PP) is still on the sample

figure 4.10 shows 10 layers of PEDOT that are patterned using plasma on specific locations

figure 4.11 shows the bending of TOPAS, PEDOT, PPy after drying. The blue piece of polypropylene is the base layer that was used to allow for better handling of the system.
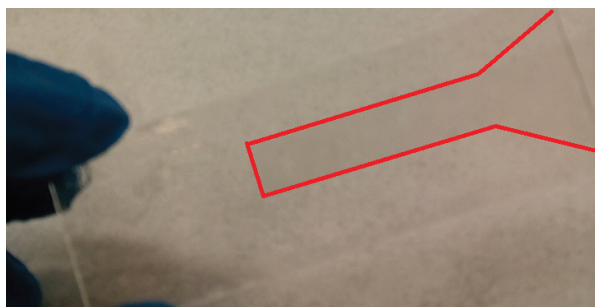

Figure 4.8: patterning using spray coating, red line added to show the patterned part
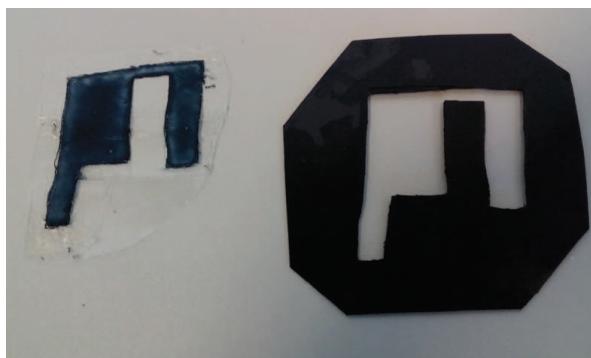
Figure 4.9: patterning using spin coating PEDOT while mask of PP

Figure 4.10: plasma patterning

PROBLEMS ENCOUNTERED

MEETINGS	date	main research	remarks
	8-4-2016	1st MSc pres	
1	14-4-2016	pdms problems, using topas?, actuation data comparison	
2	28-4-2016	training spincoating + potentiostat	no ppt available
3	12-5-2016	training SEM + ordered all chemicals+polymerization mass calculation	
4	30-5-2016	gold commercial electrode polymerization +SEM	
5	23-6-2016	making a setup for sheet testing	
6	7-7-2016	NaDBS tests gold+pedot elec.	
7	21-7-2016	polymerization on on sheet pdms/pedot + making LiTFMS	
8	04-08-2016	no pedot adhesion on pdms + thick pdms paola + selfmade thin pdms+ electrodes closer together	
9	15-09-2016	pedot+ipa+eg bath on topas sheet + 4pnt probe	using topas sheet
10	3-10-2016	new bigger tin counter electrode + thicker pedot layer + pedot/ipa/eg mix + multiple pedot layerscond.	
11	27-10-2016	testing 1-10 pedot layers ordering toluene topas	
12	10-11-2016	Making toluene topas sheets(1 layer) +pattern plasma +microfluidic ideas	
13	1-12-2016	removable coating+pp base+2xppy(dbs+TFMS)	
14	14-12-2016	different types of spinning/dripping of topas/pedot	
16	12-1-2017	trying to keep ppy in liquid/no oxidation	
18	6-2-2017	making planning to finish	
19	15-02-2017	timeline + plan A done + planning	

Figure 4.12: plasma patterning

Figure 4.11: Bending of an actuator when removed from PP layer

figure 4.12 shows the coach meetings, together with the discussed topics.

4.2. PROTOCOLS

PDMS

sylgard 184
2 components with the ratio of 10:1
spincoating for non-documented layer thicknesses, mainly used for adhesion attempts.

TOPAS-TOLUENE

dissolving 15 percent TOPAS in 85 percent toluene:
Adding the TOPAS granules to the toluene (all in fumehood) in glass bottle
Using ultrasonic machine in 15min time periods, stirring with wooden stick between cycles.
Repeat around 5 times until dissolved(or leave overnight)
spincoating/dripping TOPAS toluene:
Add toluene using a wooden stick to the sample (glass or polypropylene sheet)
Spincoating machine in fumehood, spin coating or dripping,
leave for a few hours/overnight to dry in fumehood, then for few hours in oven below glass transition temperature of TOPAS

Figure 4.13: danger indications Toluene

figure 4.13 shows the material safety data sheet danger indications.

PEDOT-PSS

PEDOT-PSS stored in the fridge.
Filtered in clean room paper before use to remove small particles contamination's.
PEDOT-PSS 1.3wt
my mixture: 100:20:5 of pedotpss:ipa:eg
(ipa=isopropanol, eg=ethylene glycol)
using plasma for 1 minute at 60 watt, then spin coating in 15 min or less.
best results of sin coating with >1000 rpm and small test pieces(<3cm)
drying at 40 degrees for 30-60 min

SECTION 2: Hazards identification

2.1   Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008
Flammable liquids (Category 3), H226
Acute toxicity, Oral (Category 3), H301
Acute toxicity, Inhalation (Category 4), H332
Serious eye damage (Category 1), H318

For the full text of the H-Statements mentioned in this Section, see Section 16.

Classification according to EU Directives 67/548/EEC or 1999/45/EC
T   Toxic   R10, R20, R25, R41

For the full text of the R-phrases mentioned in this Section, see Section 16.

2.2   Label elements

Labelling according Regulation (EC) No 1272/2008
Pictogram

Signal word   Danger

Hazard statement(s)
H226   Flammable liquid and vapour.

H301   Toxic if swallowed.
H318   Causes serious eye damage.
H332   Harmful if inhaled.

Precautionary statement(s)
P280   Wear protective gloves/ eye protection/ face protection.
P301 + P310   IF SWALLOWED: Immediately call a POISON CENTER or doctor/ physician.
P305 + P351 + P338   IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

Supplemental Hazard   none
Statements

Other hazards - none

Figure 4.14: danger indications pyrrole

Pictogram

Signal word   Danger

Hazard statement(s)
H301 + H311   Toxic if swallowed or in contact with skin
H314   Causes severe skin burns and eye damage.
H373   May cause damage to organs through prolonged or repeated exposure.
H412   Harmful to aquatic life with long lasting effects.

Precautionary statement(s)
P273   Avoid release to the environment.
P280   Wear protective gloves/ protective clothing/ eye protection/ face protection.
P301 + P310   IF SWALLOWED: Immediately call a POISON CENTER or doctor/ physician.
P305 + P351 + P338   IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P310   Immediately call a POISON CENTER or doctor/ physician.

Supplemental Hazard   none
Statements

Other hazards - none

Figure 4.15: danger indications LiTFSI

2.1   Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008
Acute toxicity, Oral (Category 4), H302
Skin irritation (Category 2), H315
Serious eye damage (Category 1), H318

For the full text of the H-Statements mentioned in this Section, see Section 16.

2.2   Label elements

Labelling according Regulation (EC) No 1272/2008
Pictogram

Signal word   Danger

Hazard statement(s)
H302   Harmful if swallowed.
H315   Causes skin irritation.
Aldrich - 289957

H318   Causes serious eye damage.

Precautionary statement(s)
P280   Wear eye protection/ face protection.
P301 + P312 + P330   IF SWALLOWED: Call a POISON CENTER/doctor if you feel unwell.
                                   Rinse mouth.
P305 + P351 + P338 + P310   IF IN EYES: Rinse cautiously with water for several minutes. Remove
                                   contact lenses, if present and easy to do. Continue rinsing. Immediately
                                   call a POISON CENTER/doctor.

Supplemental Hazard   none
Statements

2.3   Other hazards
This substance/mixture contains no components considered to be either persistent, bioaccumulative and
toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

Figure 4.16: danger indications NaDBS

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