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### Bottom-up microfabrication process for individually controlled conjugated polymer actuators

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## Bottom-up microfabrication process for individually controlled conjugated polymer actuators

### Abstract

Handling of soft and fragile sub-millimeter sized samples such as cells and tissues requires new tools that allow delicate manipulation. Conducting polymer actuators show unique characteristics suitable to driving such manipulators, however despite their potential, the current fabrication method of the trilayer structures does not allow constructing advanced micromanipulators operating in air using this technology. Here we show a novel bottom-up microfabrication process for conjugated polymer trilayer actuators using various solid polymer electrolytes. In addition, the process design integrates contact pads, which has been an issue for small scale conducting polymer actuators. The microfabrication process starts with a patterned layer of conjugated polymer, followed by depositing a polymer electrolyte and a second patterning of the second conjugated polymer layer. The process resulted in successful fabrication of individually controllable conducting polymer trilayer actuators comprising poly(vinylidene fluoride) and poly(vinylidene fluoride-co-hexafluoropropylene) membranes and showed good interfacial adhesion between the different layers in the final device. The poly(vinylidene fluoride) trilayer actuator showed good actuation capability. The developed bottom-up microfabrication method paves the way for the development of novel micromanipulation tools.

### Keywords

controlled, polymer, individually, actuators, process, conjugated, microfabrication, up, bottom

### Disciplines

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# 1 Bottom-up microfabrication process for 2 individually controlled conjugated 3 polymer actuators

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## 12 ABSTRACT

13 Handling of soft and fragile sub-millimeter sized samples such as cells and tissues requires  
14 new tools that allow delicate manipulation. Conducting polymer actuators show unique  
15 characteristics suitable to driving such manipulators, however despite their potential, the  
16 current fabrication method of the trilayer structures does not allow constructing advanced  
17 micromanipulators operating in air using this technology. Here we show a novel bottom-up  
18 microfabrication process for conjugated polymer trilayer actuators using various solid  
19 polymer electrolytes. In addition, the process design integrates contact pads, which has been  
20 an issue for small scale conducting polymer actuators. The microfabrication process starts  
21 with a patterned layer of conjugated polymer, followed by depositing a polymer electrolyte  
22 and a second patterning of the second conjugated polymer layer. The process resulted in  
23 successful fabrication of individually controllable conducting polymer trilayer actuators  
24 comprising Polyvinylidene fluoride and Poly(vinylidene fluoride-co-hexafluoropropylene)  
25 membranes and showed good interfacial adhesion between the different layers in the final  
26 device. The Polyvinylidene fluoride trilayer actuator showed good actuation capability. The  
27 developed bottom-up microfabrication method paves the way for the development of novel  
28 micromanipulation tools.

## 29 Highlights

- 30
- 31 • Bottom up microfabrication of trilayer actuators demonstrated
  - 32 • Integrating contact pad design for small scale devices
  - 33 • First working actuator for this fabrication approach

## 33 Keywords

- 1 Polypyrrole; Actuator; Solid polymer electrolyte; Electroactive polymer, Bottom up
- 2 microfabrication
- 3 Abbreviations
- 4 CP: Conjugated polymers
- 5 MEMS: Microelectromechanical systems
- 6 PVDF: Polyvinylidene fluoride
- 7 PVDF-HFP: Poly(vinylidene fluoride-co-hexafluoropropylene)
- 8 PEO: Polyethyleneoxyde
- 9 PC :Propylene carbonate
- 10 LiTFSI: Lithium bis(trifluoromethane)sulfonimide
- 11 EMITFSI: 1,3-ethylmethyimidazolium bis(trifluoromethane)sulfonimide
- 12 AIBN: Azobisisobutyronitrile
- 13 DMF: Dimethylformamide
- 14 PEGDM: Poly(ethylene glycol)dimethacrylate
- 15 PEGM: Poly(ethylene glycol)methylethermethacrylate
- 16 IPN: Interpenetrating polymer network
- 17 PPY: Polypyrrole
- 18 SPE: Solid polymer electrolyte

## 19 **1. Introduction**

20 Soft robotics is changing the way we look at robots. A paradigm shift is occurring where hard  
21 and rigid robots are intended to be replaced by soft or biomimetic robots to assure safe  
22 interaction with humans and its working environment. Soft and compliant actuators are being  
23 developed to articulate soft robotic systems. Likewise, soft microrobots and  
24 micromanipulation devices need similar soft and compliant actuators. The handling and  
25 manipulation of small, sub-millimeter-sized objects under a microscope, micromanipulation,  
26 is generally difficult to undertake with manipulation devices made of hard components and  
27 requires specialized instruments. Commercial micromanipulators exist, for instance, to probe  
28 electrical contacts or manipulate cells or small pieces of tissue. A well-known example of  
29 micromanipulation in medicine is the *in vitro* fertilization technique intracytoplasmic sperm  
30 injection. Today, this is realized with a mechanical micromanipulator adjusting rigid pipettes  
31 and vacuum suction under optical microscopes to manipulate egg and sperm cells. These  
32 methods which require manually handling samples by well-trained operators may lead to

1 challenges in reproducibility of the manipulation. Moreover, when the objects are fragile or  
2 soft, it becomes even more cumbersome and it may not be possible to handle the objects  
3 anymore using vacuum suction. Therefore, new, automated tools are needed to handle fragile,  
4 soft objects and tissues and to reduce the use of human manual handling. Throughout the  
5 years, different concepts to grasp small objects have been presented in the literature. For  
6 instance various MEMS (microelectromechanical systems) grippers have been developed but  
7 they are complex to micro-fabricate, brittle, non-compliant and display small deflections [1-  
8 4]. An interesting concept is the use of the jamming effect of granular materials for a gripper  
9 which can grab objects with arbitrary shapes [5]. However, this kind of jamming devices are  
10 difficult to micro-fabricate and would not allow grabbing soft objects. Rotary micromotors [6,  
11 7], which are difficult to miniaturize, would require a transmission mechanism such as a gear  
12 box or push/pull wires to operate a gripper and are non-compliant. Thus, there is a need to  
13 develop new micromanipulation tools in cell-biology and medicine as well as to manipulate  
14 fragile objects in general.

15 Active materials that drive such new micromanipulators should be easy to microfabricate,  
16 have accurate position control and have compliant mechanical properties to avoid damaging  
17 the sample while at the same time producing enough force to displace objects such as cells  
18 and tissue. In case of untethered applications, the materials should also have low energy  
19 consumption. Conjugated polymers (CPs) are soft smart materials that can be used to design  
20 soft actuators with a low foot-print [8-11]. It is a very promising technology since, depending  
21 on the materials structures and components, the actuators can operate in liquid, in air and in  
22 low pressure environments [12-15]. They present large actuation amplitudes while requiring  
23 low voltages in the range of 1-5V. CPs meet the requirements as actuators for soft,  
24 micromanipulation devices as they have been shown to dispense enough force ( $\mu\text{N}$ )[16] and  
25 displacement for micromanipulation and microrobotics. Although the energetic efficiency of  
26 CP actuators is low ( $\approx 1\%$ ) in comparison to piezoelectric ceramics actuators which are often  
27 used in microscale applications, they output a larger displacement [17-19]. CP actuators can  
28 be integrated into flexible electronic arrangements such as microfluidic systems.

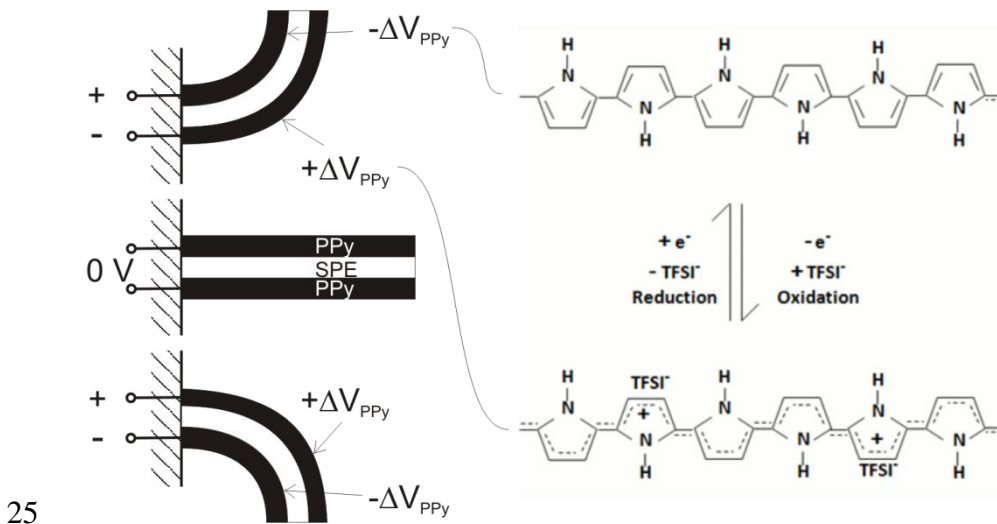
29 CPs can be microfabricated [13, 17], even into complex microrobotic arms [18]. However, all  
30 of these systems required operation in a liquid environment.

31 In 2009, it was demonstrated that using a laser ablation system, it is possible to fabricate  
32 micro-sized CP actuators generating a displacement in air [19]. Next, using classical  
33 microfabrication methods such as photo-lithography and reactive ion etching, it has been  
34 shown that it is possible to collectively microfabricate them in parallel [20]. By decreasing the  
35 size of the actuators to the microscale, the fundamental resonance frequency of the one end  
36 clamped, the other end free beam (i.e. cantilever beam) increases. Hence, it has been possible  
37 to increase the operating frequency of these systems to 1000Hz, unusually high for an ionic  
38 device [21].

39 However, due to the presence of two conjugated polymer electrodes in the trilayer structure  
40 (one on the “backside” and one on the “front”), it has been impossible until now to  
41 microfabricate a complex device with at least two individually controlled trilayer

1 microactuators operating in air. Moreover, the size of the microbeam makes it difficult to  
 2 place the clamp that also acts as an electrical contact. Recently, it has been shown that by  
 3 patterning the gold electrodes on polyvinylidene fluoride (PVDF) commercial porous  
 4 membranes, it is feasible to fabricate individually addressable trilayer actuators using  
 5 microfabrication technology. [22] However, this methodology is not suitable for microscale  
 6 engineering since it uses thick PVDF membrane. In addition, the substrates need to be flipped  
 7 during the fabrication process in order to pattern both electrodes making the alignment  
 8 difficult across an optically opaque layer. An alternative solution to the etching of Au  
 9 electrodes would be the etching of the conjugated polymer layer in conducting  
 10 interpenetrating polymer networks. However, this method would still require flipping the film  
 11 and would result in inhomogeneity in the thickness of materials making it difficult to model.  
 12 For these reasons, we developed a bottom-up microfabrication process with different polymer  
 13 electrolytic membranes, designing a layer by layer polymerization method in a classical  
 14 microfabrication process [23] inspired by the microfabrication methods used to produce an  
 15 articulated microrobotic arm [18].

16 The working principle and the structure of the CP trilayers actuators is shown in figure 1. The  
 17 structure is composed of one solid polymer electrolyte (SPE) acting as an ion reservoir  
 18 between two CP electrodes. When a voltage is applied between the two CP electrodes, one  
 19 electrode is oxidized while the other is reduced. The oxidation-reduction process is  
 20 accompanied by an ion motion to compensate the charge created on the polymer backbone  
 21 and thus keep electroneutrality. The ion movement causes a net volume change in the two  
 22 electrodes layers leading to the bending of the trilayer device. This bending is fully reversible.  
 23 For more details on the functioning of CP trilayer actuators, we refer to Zhou *et al* [24] and  
 24 Vidal *et al* [25].



25

26

27 Fig. 1: Principle of conjugated polymer bending actuators based on the oxidation reduction  
 28 process of PPy.

29

1 Typically, for CP actuators, commercial porous PVDF membranes (such as Kynar® or  
2 Immobilon-P® membranes) are used as SPE. These commercial membranes are fabricated  
3 by phase inversion method. However they are not compatible with a bottom-up  
4 microfabrication process as they are too thick and required flipping of the substrate [22].  
5 Gaihre et al have nevertheless shown that using porogens in PVDF solution, it was possible to  
6 fabricate thin ionic conductive porous PVDF membrane for actuators fabrication.[26] Other  
7 interesting strategies to obtain high conductive membranes can be plasticising PVDF with  
8 polymethylmethacrylate in a blend[27], or mixing PVDF-HFP with ionic liquid to produce a  
9 highly conductive ionic gel.[28, 29] Indeed the latter has been even used to develop the  
10 carbon nanotube based bucky-gel actuators.[29] However, in both of these cases, since the  
11 electrolyte is already contained in the membrane and that the patterning of top gold layer and  
12 successive electropolymerization required solution processing, the ionic liquid would diffuse  
13 out of the membrane and the amount of ionic liquid would be difficult to control preventing  
14 reproducibility of the work. An alternative strategy to obtain SPE membranes for CP actuators  
15 has been to synthesize interpenetrating polymer networks (IPNs). An IPN is the combination  
16 of two or more polymer networks synthesized in juxtaposition, which can be used to combine  
17 antagonist properties and functionalities [30]. IPNs result in SPEs that give both a high ionic  
18 conductivity as well as good mechanical properties such as high elongation at break [31].  
19 Semi-IPN, which is the combination of one polymer network with one linear polymer, have  
20 been used for a top-down approach for the direct synthesis and patterning of CP actuators on  
21 flexible substrates.[30] In this study, we present a newly conceived bottom-up micro-  
22 fabrication process for CP actuators and evaluate various SPE membranes for bottom-up  
23 fabrication process.

## 24 **2. Materials and Methods**

### 25 **2.1. Materials**

26 Pyrrole was obtained from Sigma–Aldrich, distilled and stored at  $-18\text{ }^{\circ}\text{C}$  prior to usage.  
27 Propylene carbonate (PC) and bis(trifluoromethane)sulfonimide lithium salt (LiTFSI), PVDF  
28 (powder,  $M_n=534000\text{ g}\cdot\text{mol}^{-1}$ ), PVDF-HFP (polyvinylidene fluoride-co-hexafluoropropylene,  
29 pellets,  $M_n=110000\text{ g}\cdot\text{mol}^{-1}$ ) and dimethylformamide (DMF) (Sigma–Aldrich) were used as  
30 received.  $\text{I}_2$ , KI were acquired from Merck and used as received. Photoresist S1818 and  
31 corresponding developer microposit 351 (to dilute) were acquired from Microchem  
32 corporation.  $4''$  Si 100 wafer were obtained from semiconductor wafer, Inc.  
33 Azobisisobutyronitrile (AIBN) was recrystilized in methanol prior to use, cyclohexanone  
34 (Acros, 99.8%), poly(ethylene glycol) dimethacrylate. (PEGDM,  $M_n = 750\text{ g mol}^{-1}$ , Aldrich),  
35 poly(ethylene glycol) methyl ethermethacrylate (PEGM,  $M_n = 475\text{ g mol}^{-1}$ ) were purchased  
36 from sigma-Aldrich. Nitrile butadiene rubber with 44 wt% acrylonitrile content was obtained  
37 from Lanxess.

### 38 **2.2 Methods**

39

## 1 **Microfabrication**

2 Microposit S 1818 photoresist was spin-coated at 4000rpm/4000rpm.s<sup>-1</sup> during 30s using a  
3 POLOS spincoater and baked in an oven at 100°C during 20 minutes. The photoresist was  
4 then exposed for 10 s using a UV source at 365 nm, :10 mJ.cm<sup>-2</sup> intensity, using a Karl Suss  
5 MJB-3 mask aligner with a printed photomask from Acreo AB, Norrköping, Sweden. Next  
6 the exposed parts were developed using Microposit 351 developer solution.

7 Gold etchants solution (KI/I<sub>2</sub> aqueous solution) was prepared by dissolving 4 g KI and 2 g I<sub>2</sub>  
8 in 100 ml H<sub>2</sub>O.

9 The first gold layer is evaporated using an in-house built thermal evaporator at a rate of 5 Å/s  
10 at a pressure of 2 mTorr. The second gold layer was deposited using a Vacutec  
11 PlasmaSystems sputter system at a pressure of 1.8 mTorr, 26.0 cm<sup>3</sup>min<sup>-1</sup> Ar flow during 5  
12 minutes resulting in a layer of 400Å.

## 13 **Electropolymerisation**

14 Polypyrrole (PPy) layer is electrodeposited in a two electrode configuration at a constant  
15 current of 0.1 mA.cm<sup>-2</sup> using an Ivium compactstat or IviumStat (Ivium Technologies,  
16 Eindhoven, The Netherlands) on the patterned gold electrodes from a 0.1 M Pyrrole, 0.1 M  
17 LiTFSI and 1 % water in a carbonpropylene solution for 2 hours at -18 °C. A stainless steel  
18 mesh was used as the counter electrode.

## 19 **Preparation and deposition of solid polymer electrolyte (SPE):**

20 PVDF or PVDF-HFP polymers are solubilized in DMF at 200 and 100g.L<sup>-1</sup> respectively.  
21 These solutions were spin-coated on a substrate using a POLOS spincoater, followed by  
22 drying at 50 °C during 30min to form a film. In order to obtain pores into the PVDF  
23 membrane, an inversion method was used [31]. After spin-coating, and a delay of 5s, the  
24 substrate is immersed into a water bath cooled down to 5°C.

25 To prepare polyethyleneoxide-PVDF (PEO-PVDF) semi-interpenetrating polymer network  
26 (semi-IPN), first PVDF (1g) was dissolved in DMF (5g) and then PEGM (0.5g), PEGDM  
27 (0.5g) and 30 mg of AIBN were added to the solution. The mixture was then stirred under  
28 nitrogen for 30 min, before spincoating the solution at 500rpm onto the substrate and  
29 polymerizing the film for 12 hours at 80°C under nitrogen atmosphere.

30 A similar procedure was used to synthesize a PEO-NBR semi IPN. First 1g of NBR was  
31 dissolved in 5g cyclohexanone during 24 hours at room temperature. Thereafter 0,5g of  
32 PEGM and 0,5g of PEGDM were added to the solution with 30 mg of AIBN. The mixture  
33 was then stirred under nitrogen for 30 min, spincoated onto a substrate at 500rpm and  
34 polymerized for 12 hours at 80°C, under nitrogen atmosphere.

35 The polymer solutions of PVDF, PVDF-HFP and of the precursors of NBR-PEO and PVDF-  
36 PEO semi-IPNs were spin-coated onto a silicon wafer (with CP pattern or not) at  
37 500rpm/500rpm.s<sup>-1</sup> during 30s. Then, a curing step respective to each materials followed the  
38 deposition.



## 1 **Measurements:**

2 Profilometry measurements (Dektak 6M) were used to get the thicknesses of the different  
3 materials.

4 The actuators were electrically addressed using a compactstat or IviumStat (Ivium  
5 technologies) connected using 2mm stainless steel crocodile clips on the contact pads,  
6 external to the actuators. The displacement was followed by a laser displacement sensor,  
7 optoNCDT 1700-50 from Microepsilon (Ortenburg, Germany).

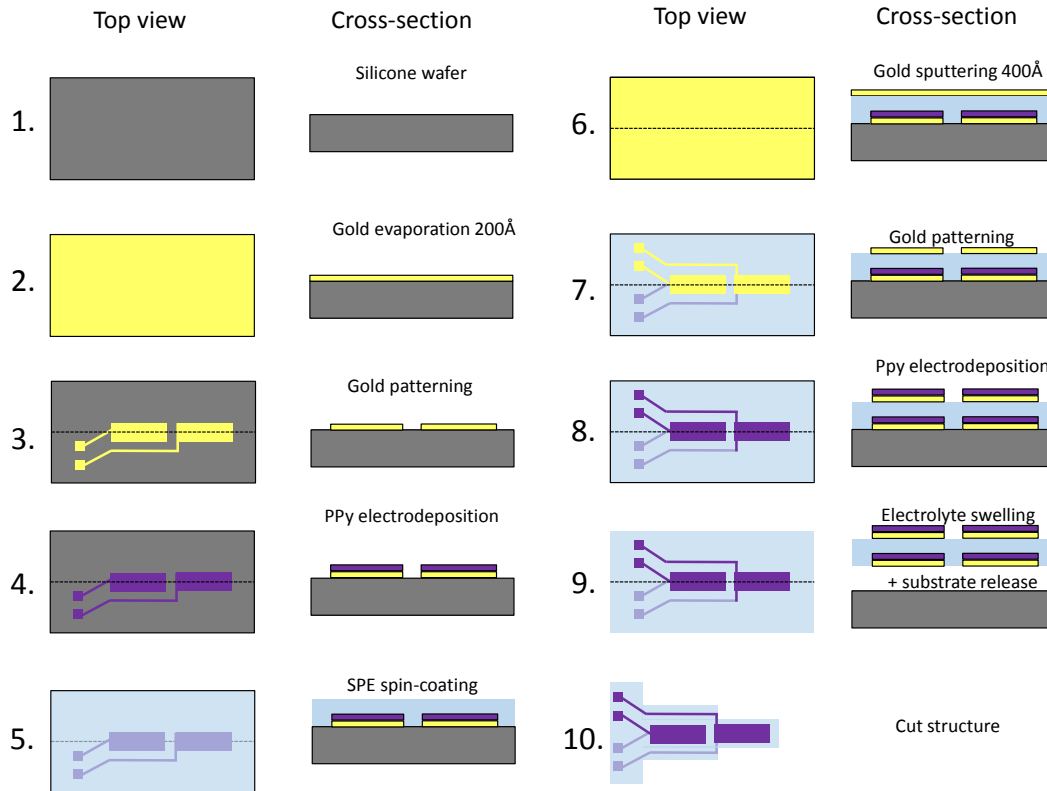
8 The ionic conductivity of the swollen material was measured in a two-electrode system by the  
9 complex impedance method using an impedance analyser (Autolab PGSTAT30 with a  
10 Frequency Response Analyser module FRA2 from Metrohm). The experiments were  
11 performed for an applied peak potential of 5mV in the frequency range from 0.01 Hz to 100  
12 MHz at 25 °C. The film was put in a cell with pressure contact stainless steel electrodes.

## 13 **3. Results and discussion**

### 14 **3.1 General bottom-up microfabrication process**

15 A classical lithography process was used to pattern two individually controlled actuators. The  
16 process flow is shown in figure 2. A gold layer of 500Å was evaporated onto the silicon  
17 substrate. Photoresist was used to pattern the gold layer and the exposed gold surface was wet  
18 chemically etched in a KI/I<sub>2</sub> aqueous solution resulting in a first pattern of the bottom  
19 electrodes including the contacts pad. Next, the first, bottom polypyrrole (PPy) layer was  
20 electropolymerised. A two electrode set-up was used for the electrosynthesis: the patterned  
21 Au electrode was connected to the working electrode lead of the potentiostat and a stainless  
22 steel mesh was used as the counter electrode. The reference electrode lead was connected to  
23 the counter electrode. The obtained thickness of the PPy layer was ~ 8µm. A SPE was then  
24 spin-coated onto the first PPy layer, followed by the appropriate curing step (See section 2.2  
25 for more details about each membrane). The second, top, gold layer was sputtered, resulting  
26 in a layer of 400Å. The patterning of the second electrode was realized in the same way as the  
27 first. The second PPy layer was then synthesised using the same conditions as the first one. To  
28 finish the actuator fabrication, the wafer was immersed in the electrolytic solution of 0.1 M  
29 LiTFSI in propylene carbonate a room temperature to swell the SPE and release the device.  
30 Finally the actuators were manually cut out using a scalpel.

31



1

2 Fig. 2: Process flow for the fabrication of the individually controlled actuators. Step 1 to 4:  
 3 deposition of 1<sup>st</sup> patterned CP electrode. Step 5: deposition of SPE material. Step 6 to 8:  
 4 deposition of the second patterned CP electrode. Step 9: swelling of the materials by the  
 5 electrolyte and release of the trilayer structure from the substrate. Step 10: cutting the trilayer  
 6 structure.

7 We investigated the feasibility of using this bottom-up microfabrication process with different  
 8 SPE materials. The swelling ratio of LiTFSI/Propylene carbonate 0.1 M electrolyte, the ionic  
 9 conductivity, and the advantages and drawbacks of each membrane towards this bottom up  
 10 microfabrication process are summarized in Table 1.

11 Table 1: Properties of selected SPE materials

Material	Swelling ratio (wt.%)	$\sigma$ (S.cm <sup>-1</sup> )	Drawback	Advantage	Result
<b>PVDF</b>	55	10 <sup>-6</sup>	Low ionic conductivity	Easy to process using spin-coating	Final device
<b>PVDF-HFP 110</b>	46	3 10 <sup>-7</sup>	Low ionic conductivity	Easy to process using spin-coating	Final device

<b>PVDF + pores by phase inversion method</b>	--	--	Adhesion to the substrate, Shrinking during the precipitation of PVDF	Presumably high ionic conductivity	SPE Membrane deposition only
<b>Phase separated PEO-PVDF semi IPN</b>	575	$1.5 \cdot 10^{-4}$	Macroscopic phase separation	High ionic conductivity	SPE Membrane deposition only
<b>NBR-PEO semi IPN</b>	350	$10^{-3}$	Swelling with electrolyte at the final step lead to delamination of multi-layered device	Ionic conductivity, Processability by spin-coating	Final device but electrode delamination during electrolyte swelling step

1

## 2 **3.2 SPE processing and integration in microfabrication**

3 PVDF and PVDF-HFP membranes are used as SPE in actuators for soft microrobotics. These  
4 membranes can be easily processed using spin-coating and thermal curing which are common  
5 methods employed in microfabrication. As such, we have been able to integrate both SPEs in  
6 functional trilayer devices (See Sect. 3.3) However, these membranes exhibit a low ionic  
7 conductivity in presence of an electrolyte (respectively  $10^{-6}$  and  $3 \cdot 10^{-7}$  S.cm<sup>-1</sup> for PVDF and  
8 PVDF-HFP swollen membranes). Therefore, we also synthesized some new ionic conductive  
9 membranes for actuators by a physical method or by chemical engineering.

10 One way to increase the conductivity is to employ a more porous membrane. We synthesised  
11 a porous PVDF membrane by a phase inversion method. In this method, the DMF diffuses out  
12 of the PVDF while water penetrates, thus creating a porous structure. At the same time, the  
13 PVDF precipitates onto the substrate forming a film. When the PVDF film precipitated on the  
14 substrate, a high lateral shrinking was observed often causing a delamination from the  
15 underlying substrate, including the first patterned layer. Also, the pores' sizes were relatively  
16 large thus preventing the SPE membrane to fully cover the underlying rough PPy layer (see  
17 figure 3). These effects prevents the formation of the second patterned electrode in the  
18 actuator fabrication process. The porous PVDF SPE made by phase inversion method is an  
19 interesting candidate, but requires more development.



20

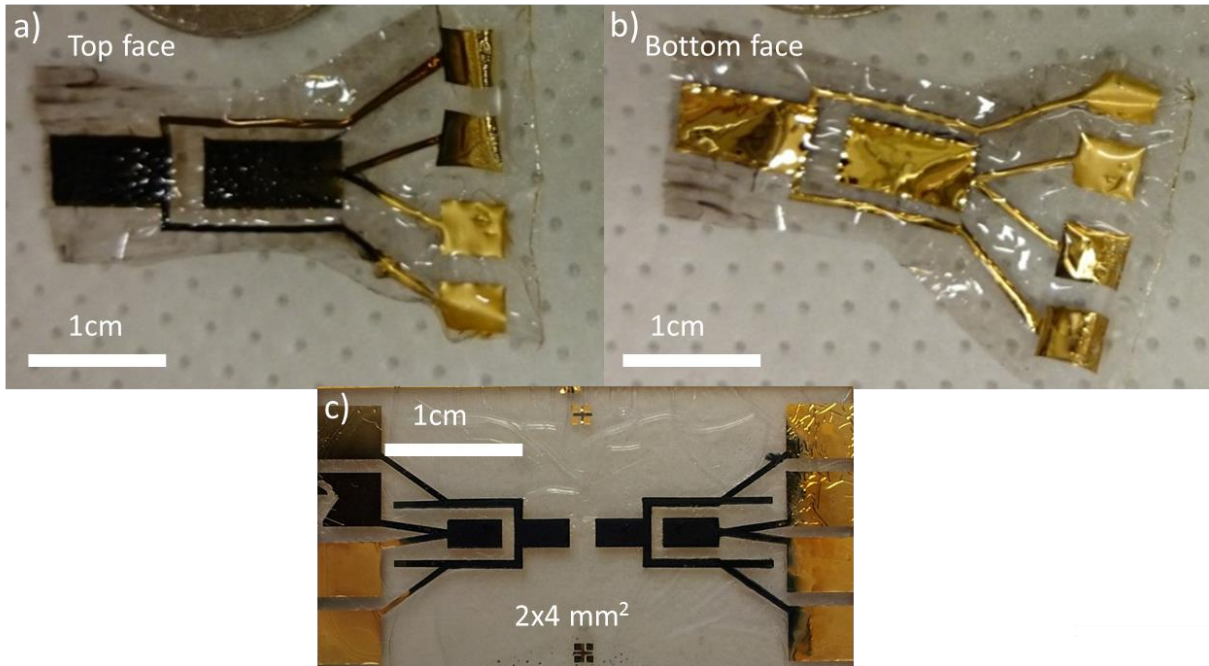
1 Fig 3: Delaminated porous PVDF made by phase inversion method.

2 Next, we synthesized a new semi-IPN based on PVDF physically crosslinked by its  
3 crystallites and the PEO network. The material can be processed using spin-coating and cured  
4 at 80 °C in presence of AIBN. The measured ionic conductivity of this this semi-IPN material  
5 was high enough ( $1.5 \cdot 10^{-4} \text{ S.cm}^{-1}$ ) to establish a multi-layer bending actuator. However,  
6 macroscopic phase separation in the material occurred, leading to internal stress, causing the  
7 multilayer device to curl around itself and delaminate the substrate during the swelling. We  
8 believe that this is a promising material and that through more elaborate synthesis study, it  
9 may be possible to avoid this phase separation to achieve excellent SPE material properties.

10 NBR-PEO IPN is often used as the SPE in ionic actuators synthesis, however it cannot be  
11 used in this bottom-up microfabrication as the vulcanization of NBR requires a high  
12 temperature (180°C) that would damage the underlying PPy. Therefore, NBR-PEO semi-IPNs  
13 were used where only the PEO network is crosslinked at 80°C, allowing a compatible  
14 deposition of this membrane with the bottom-up microfabrication process. Lastly, the PEO-  
15 NBR semi-IPN was then tested with this process. It is an excellent SPE membrane showing  
16 excellent properties such as a high ionic conductivity of  $10^{-3} \text{ S.cm}^{-1}$  when the material is  
17 swollen by LiTFSI/PC or EMITFSI electrolytes. It was possible to go through all the steps of  
18 the process and microfabricate the trilayer structure comprising individual electrodes.  
19 However, when the material was immersed in the electrolyte, it reached a high weight  
20 swelling ratio of 350% leading to a high volume change of the membrane, causing internal  
21 stresses at the gold/PPy-SPE interface causing a delamination of the active parts (Au and PPy)  
22 from the SPE.

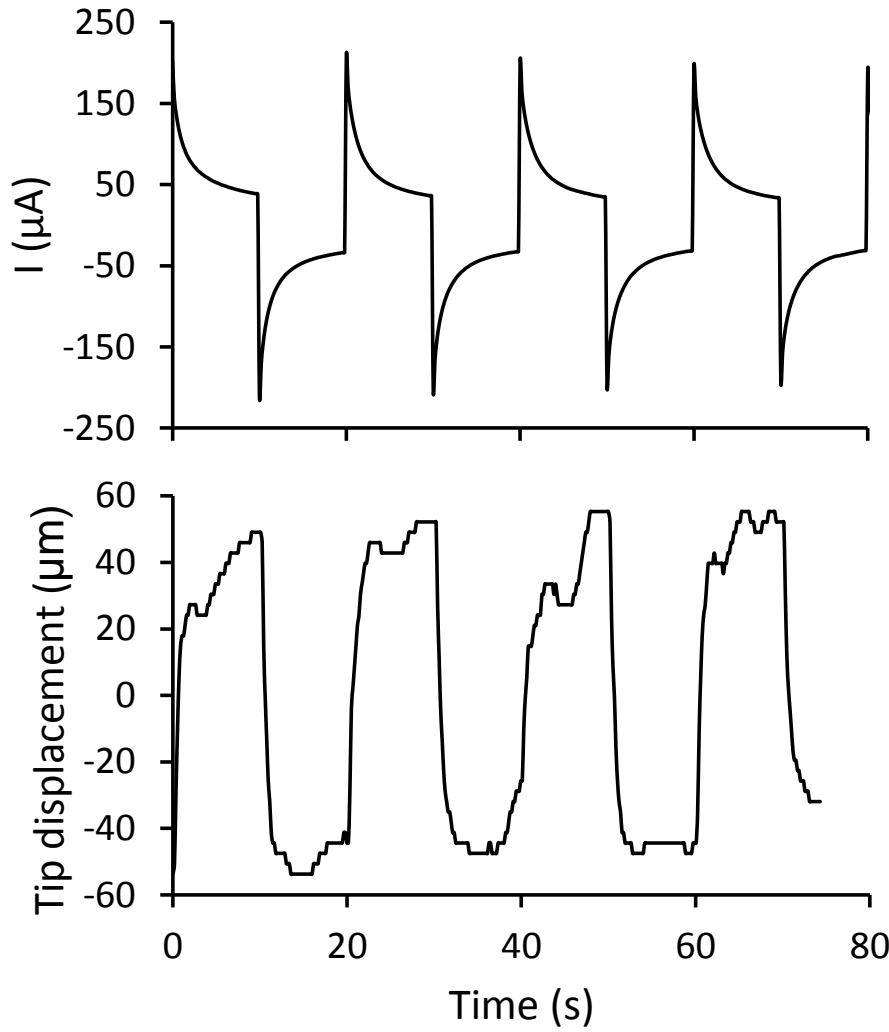
### 23 **3.3 Trilayer actuator fabrication**

24 Using PVDF or PVDF-HFP membranes as the SPE, we were able to successfully process the  
25 individually addressable trilayer actuator device using the bottom-up microfabrication  
26 process. The final devices are presented in figure 4. We made two different designs each  
27 having two individually addressable PPy trilayer actuators of either  $5 \times 10 \text{ mm}^2$  or  $2 \times 4 \text{ mm}^2$ .  
28 The photographs in figure 4 show good resolution of the achieved patterning, thus enabling,  
29 in combination with laser ablation techniques, future downscaling to decrease the size of the  
30 device to a microscale and the possibility of producing individually controlled microactuators.  
31 Moreover, it was possible to add the contact pads for these two actuators. After swelling in  
32 the electrolytic solution, the devices were cut out and the actuation characteristics of the built  
33 devices were tested.



1

2 Fig 4: Bottom-up fabricated actuator devices (or “fingers”) with individually addressable PPy  
3 trilayer actuators with 34  $\mu\text{m}$  thick PVDF membrane manually cut with a scalpel: a) top face  
4 and b) bottom face of a device comprising two  $5 \times 10 \text{ mm}^2$  sized PPy actuators and c) top face  
5 of two devices each comprising two  $2 \times 4 \text{ mm}^2$  sized PPy actuators.



1

2 Fig 5. Actuation current and displacement of addressing ( $\pm 1$  V) one of the  $5 \times 10 \text{mm}^2$  actuators  
 3 of a device.

4 Figure 5 shows the actuation current and displacement when addressing one of the  $5 \times 10 \text{mm}^2$   
 5 actuators of a device. A tip displacement of  $100 \mu\text{m}$  was measured at  $10 \text{mm}$  from the contact  
 6 when  $\pm 1$  V was applied at a frequency of  $0.05 \text{Hz}$ . From this deflection, the corresponding  
 7 strain of  $10^{-2}\%$  is calculated from the following expression for the strain at any location along  
 8 the actuator length  $L$ ;

9 
$$\varepsilon = 2 \frac{h(L-x)^2}{L^4} y_{tip}, \text{ for } x=0, \quad \varepsilon = 2 \frac{h}{L^2} y_{tip} \quad (1)$$

10 where the variable  $x$  starts from the fixed end of the actuator,  $h$  and  $y_{tip}$  are the total thickness  
 11 of the actuator and tip displacement of the actuator in the transverse direction, respectively.  
 12 Eq. 1 assumes that the actuator is modelled as a cantilever beam under a uniformly distributed  
 13 load [26, 32]. This tip displacement of  $100 \mu\text{m}$  is small when compared with the capabilities  
 14 of such conjugated polymer materials. For instance, Gaihre *et al* achieved  $1.5 \%$  strain  
 15 applying only a potential of  $0.5 \text{V}$  on thin actuators [26]. We believe this is due to the low

1 ionic conductivity of the membrane preventing the ions to be inserted and ejected from the  
2 active layer, resulting in as well a limitation of the working frequency. Indeed, if ion motion is  
3 restricted, the oxidation-reduction reaction is reduced, thus limiting the volume change and  
4 bending of the actuators. To investigate this hypothesis, the actuator device was operated in a  
5 0.1 M LiTFSI/PC solution, which functions as an external electrolyte and ion source/sink.  
6 Inserted in the external electrolyte the devices showed the typical large displacement (~10  
7 mm) of CP actuators (indicating a high strain), confirming that there is a problem with the  
8 migration of the ions from the electrolytic polymer membrane towards the CP layers.  
9 Unfortunately, our study for better ionically conductive membranes compatible with the  
10 bottom-up fabrication process has not yet resulted in finding a SPE membrane for these  
11 devices, but both semi-IPN SPEs are very promising candidates that need further  
12 investigation. In addition, we are looking for a new way to synthesise flexible and stretchable  
13 electrodes. This will simplify the process and enable the use of high ionic conductive  
14 membranes with individually controlled CP actuator fabrication.

#### 15 **4. Conclusion**

16 A novel fabrication process is reported, showing the feasibility of individually addressable CP  
17 actuators operating in air using a bottom-up microfabrication process. The process is  
18 applicable to different SPE membranes. Using this process, we have successfully made  
19 functional PPy trilayer devices comprising individually addressable actuators. However, the  
20 attained displacement of the actuators fabricated with the PVDF as the SPE membrane was  
21 smaller in comparison to previously presented CP trilayer actuators [33] due to the low ionic  
22 mobility in the employed SPE. Moreover, a promising SPE semi-IPN membrane based on  
23 PVDF, polymethacrylate and polyethyleneoxide was synthesized in order to improve ionic  
24 conductivity as well as the mechanical properties (such as the Young modulus). This new SPE  
25 showed promising homogeneous characteristics in terms of ionic conductivity. An issue with  
26 the NBR-PEO semi-IPN SPE is that the gold electrodes used in the process are not stretchable  
27 and prevent the use of efficient ionic conductive membrane since the swelling causes the  
28 electrodes to delaminate. To overcome this problem and exploit this actuation capacity of the  
29 conjugated polymer, our future research will focus on synthesising stretchable electrodes to  
30 allow the use of high swollen SPE membranes. We are also currently continuing the work to  
31 further scale down the devices and fabricate individually controlled micrometer-sized PPy  
32 actuators operating in air. The developed bottom-up microfabrication method presented here  
33 paves the way for the development of novel micromanipulation tools.

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