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On-Chip Microelectrodes for Electrochemistry with Moveable PPy Bilayer Actuators as Working Electrodes

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Abstract

We present electrochemical microactuators which have all the electrodes necessary for the actuation -- the working, counter, and reference electrodes -- on-chip. This is a first step towards an all-polymer system, i.e. a system that does not require a liquid electrolyte. The microactuators' performance was as good as when standard, off-chip counter and reference electrodes were used. Specifically, the speed of actuation was the same. In addition, we obtained a good cyclic voltammogram, although the oxidation and reduction peaks were shifted and some noise was present. Apart from application in an all-polymer system, we will also use these microactuators for studies on the effect of mechanical stimulation of living cells.

Keywords: actuator, microfabrication, microelectrode, polypyrrole, electrochemistry

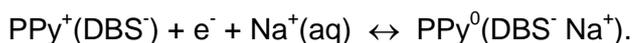
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Introduction

Microactuators have been fabricated based on a variety of different physical principles, including thermal expansion [1, 2], magnetism [3], and electrostatic forces [4]. In our laboratory, we have developed microactuators based on the reduction-oxidation reaction of the conjugated polymer polypyrrole (PPy). Using these microactuators, moving paddles and self assembling micrometer sized boxes have been demonstrated [5].

Today, our polypyrrole microactuators have one drawback: they need to be operated in a liquid electrolyte (a salt solution). Although we have successfully operated the microactuators in a number of interesting salt solutions, including blood plasma, urine, and cell medium, they are still limited to liquid environments. We are now working on a dry system, i.e. microactuators that function in an air atmosphere without a liquid. Before explaining how we want to achieve such a dry system, we will first give a short introduction to our previous microactuators. For a more thorough description of their fabrication, we refer to [6].

The microactuators are based on the volume changing ability of PPy. By applying a voltage, one can remove electrons from the PPy chains and switch the material from its neutral state (PPy⁰) to its oxidised state (PPy⁺). This process is reversible: by adding electrons one can reduce PPy from its oxidised state back to its neutral state. The oxidised state is often called the *doped* state (and the neutral state *undoped*) in analogy to the doping of silicon. The reduction-oxidation leads to a change in conductivity [7], colour [8], and volume [9]. When PPy is combined with a non-volume changing layer into a bilayer structure, this volume change can be used to make actuators [10-14]. For the microactuator, we use a layer of Au for this purpose, which also acts as an electrode. The PPy is doped with dodecylbenzenesulfonate (DBS) anions. During reduction of the PPy layer in a liquid electrolyte, cations, in our case Na⁺ (surrounded by a layer of water molecules: their hydration shell [15]), are inserted into the PPy to maintain charge neutrality in the PPy film. This causes swelling of the film and thus straightening of the bilayer. On oxidation the cations are expelled from the film, it shrinks and results in a bending motion. We can summarise this redox reaction as follows:



For PPy(DBS) we achieve the neutral state at an applied voltage of -1 V vs. Ag/AgCl and the oxidised state at 0 V. By holding the potential fixed at any potential within the two potential limits (completely oxidised or completely reduced), we can position the microactuators at any intermediate position. It is also possible to move the actuators between intermediate positions, for instance by changing from -0.4 V to -0.6 V and returning to -0.4 V.

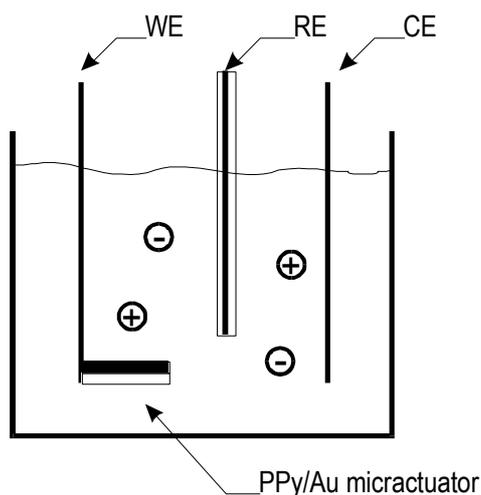


Figure 1 A sketch of a 3-electrode electrochemical cell with a microactuator as the working electrode (WE). The reference electrode (RE) is a commercial Ag/AgCl electrode and the counter electrode (CE) is an Au coated Si wafer.

Because the principle for activation of the microactuators is a reduction-oxidation reaction, the devices are operated in a three-electrode electrochemical cell. Such an electrochemical cell consists of a working electrode, a counter electrode, and a reference electrode inserted in a liquid electrolyte [16, 17]. Figure 1 shows a sketch of such a cell. The working electrode is the microactuator, at which a well defined potential is applied; this leads to a defined redox reaction, in our case the oxidation-reduction of PPy. Simultaneously, a counter redox reaction occurs at the counter electrode. The reference electrode is necessary to set a defined potential. As the electrolyte we normally use a 0.1 M solution of NaDBS. The electrolyte functions as an ion transport and storage medium. Until now, we have always used large counter electrodes (for instance an Au wire or Au coated silicon wafer) and a large commercial Ag/AgCl reference electrode (Bioanalytical Systems, Inc.).

As mentioned before, we want to achieve a “dry system” (or “all-polymer system”), i.e. without a liquid electrolyte. To achieve a dry system we need to make two modifications to the present design. First, we need to replace the liquid electrolyte by another, non-liquid ion transporting and storing layer, for instance a solid polymer electrolyte (SPE) or a gel. An SPE is a polymer that is able to conduct ions. Unfortunately, a disadvantage of SPEs is that the ion diffusion coefficients are low. This will make the actuators slow. A gel is a polymer mesh containing a liquid, for instance water, which in its turn conducts the ions. Because diffusion of the ions takes place in the liquid phase, diffusion coefficients are higher than for SPEs. The second modification necessary for a dry system concerns the positions of the working, counter, and reference electrodes. One option is to make a sandwich structure of the working and counter electrodes with the non-liquid electrolyte between, as shown in Figure 2a. In this “rocking chair” configuration, the RE channel is connected to the CE, and ions are shuttled from one PPy layer across the SPE to the other as the oxidation levels are changed. Another option is to put the three electrodes parallel on a substrate and cover them with a layer of the non-liquid electrolyte as in Figure 2b. The CE can optionally also be covered by PPy if greater ion storage capacity is required.

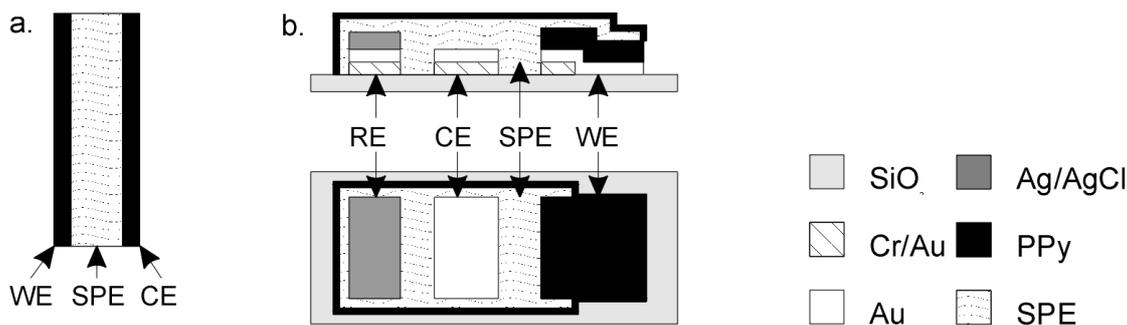


Figure 2 Two possible electrode configurations for the dry system. a. Sandwich structure in which the solid polymer electrolyte (SPE) or gel is sandwiched between WE and CE, both made of PPy. b. Parallel configuration in which the WE, CE, and RE are placed side by side on a substrate and covered with the SPE or gel.

Recently two groups have demonstrated all-polymer macro-actuators [18, 19]. Both groups have taken a similar approach: a solid polymer electrolyte (SPE) sandwiched between two conducting polymer electrodes (Figure 2a). Sansiñena *et al.* [18] used films of PPy doped with LiClO_4 as electrodes and poly(epichlorohydrin-co-ethylene oxide) containing LiClO_4 as the SPE. Although the electrolyte is an SPE, water is important in the conduction of the ions because it only works well when the humidity is high enough [20]. Lewis *et al.* [19] made the electrodes of PPy doped with pTS and NaClO_4 . As the electrolyte they used polyacrylonitrile with ethylene carbonate, propylene carbonate, and NaClO_4 . In both cases, bending of 90 degrees in both directions was achieved.

We will try a different approach to achieve a dry system. We have chosen to place the electrodes parallel on the substrate because it is not possible to deposit a second layer of PPy on top of the electrolyte. Neither can we use the fabrication method used in the macro-actuators, which consists of pressing together the separate layers to form the triple layer. As an electrolyte we intend to use a hydrogel. Arquint has presented a hydrogel that can be micropatterned by photopolymerisation [21].

A spin-off application of having all electrodes on-chip can be found in the field of cell biology. We are trying to use the microactuators as a tool for studying cells. Working with the large counter and reference electrodes under the microscope is quite cumbersome, so it would be convenient to have all the electrodes miniaturised on-chip. Also, in medicine there is a need for disposable microsensors. These microsensors require the electrodes to be on-chip.

Experimental

Fabrication of the electrodes

To form the electrodes, we started with a cleaned silicon wafer on which a $1\ \mu\text{m}$ thick silicon oxide had been thermally grown to insulate the surface. On this, we thermally evaporated $50\ \text{\AA}$ Cr and $200\ \text{\AA}$ Au. The chromium layer is necessary as an adhesion promoter, because the gold itself adheres poorly to the silicon substrate. Using standard photolithographic techniques, we etched windows in the chromium and gold layers (see Figure 3a.). These windows are necessary for the releasing step. We use a method called differential adhesion [6, 22] rather than using a sacrificial layer to release the finished actuators. Following that, we deposited a $1000\ \text{\AA}$ thick structural gold layer by thermal evaporation (Figure 3b).

In the next step we formed the Ag/AgCl reference electrodes. We covered the gold with photoresist patterned with openings to define the areas where we wanted

to electroplate Ag. In this way we directly patterned the silver layer, without the need of an etch step. (It is important to give the resist a thorough hardbake, otherwise the electroplate solution will attack the resist: the colour of the resist will turn dark red and cracks will appear. Also the Ag structures will be deformed, leading to bulges. We hardbaked the samples in an oven at 125° C for 15 minutes.) We electroplated silver from a bath solution of AgCN 40 g/l, KCN 60 g/l, K₂CO₃ 20 g/l [23]. We used our electrochemistry equipment in the galvanostatic mode (constant current), hooked the sample to the working electrode, and used an Ag wire as the counter electrode. We applied a current density of approximately -5 mA/cm² for 10 or 15 minutes. After rinsing the sample with deionized water, we partially converted the Ag layer to Ag/AgCl electrochemically. We connected the sample to the working electrode and inserted it in a 50mM KCl solution using a Pt counter electrode [21]. We applied a current density of 0.5 mA/cm² for 5 minutes. The Ag layer turned dark grey, and the total thickness of the Ag/AgCl was 4.7 μm (10 min Ag deposition) or 5.7 μm (15 min. Ag deposition) as measured with a Dektak surface profilometer. Figure 3c. schematically shows the result after removing the resist layer with acetone.

For the moveable working electrodes, we deposited polypyrrole, the active layer, (see Figure 3d). We patterned the PPy layer by partially covering the wafer with photoresist, similar to the Ag/AgCl patterning. The polymer was electropolymerized at the gold surface from a 0.1 M pyrrole, 0.1 M NaDBS solution at a voltage of 0.55 V vs. Ag/AgCl with an Au counter electrode. During the growth, the large DBS⁻ anions are incorporated in the polymer film, by which the polypyrrole becomes doped [15].

Next we removed the excess Au and underlying Cr, see Figure 3e, to define the electrodes. To protect the PPy and Ag/AgCl from the Au-etchant and especially the Cr-etchant, the photoresist overlapped these structures by 5 μm.

Experiments showed that when the leads from the electrodes to the contact pads (Figure 3e) were exposed to the electrolyte solution, a residual current was present in the cyclic voltammogram. Therefore, these leads were insulated with a resist layer with openings over the electrode sets and contact pads. After the last etching step, the moveable working electrodes/microactuators are free but still attached to the surface, ready to be released during the first redox cycles [5].

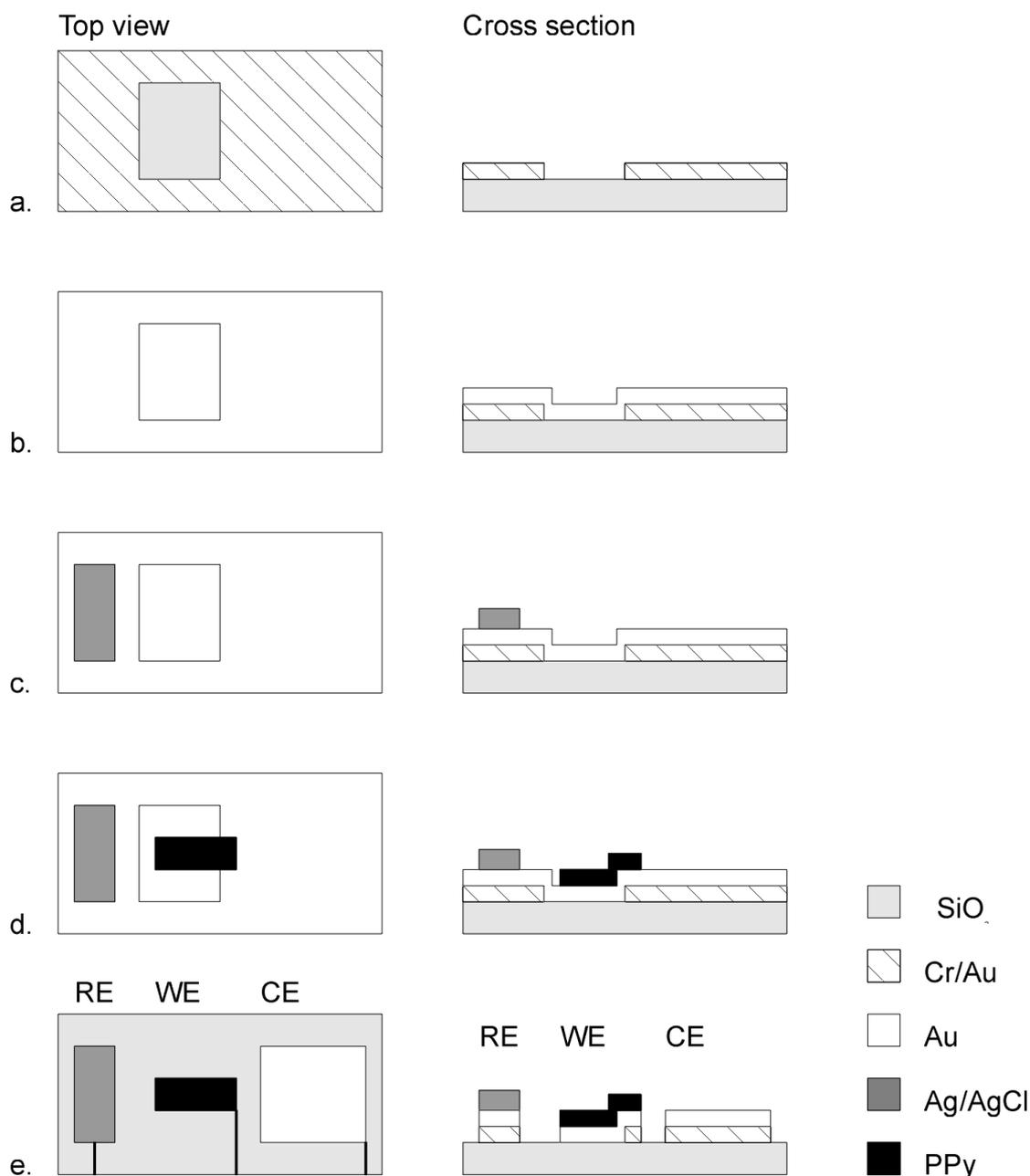


Figure 3 The process steps for the fabrication of the microactuator and the counter and reference electrodes. a. Deposit and pattern the Cr/Au adhesion layer. b. Deposit the Au structural layer. c. Deposit and pattern the Ag/AgCl. d. Deposit and pattern PPy. e. Etch Au and Cr. Now all the electrodes, leads, and contact pads (not shown) are defined.

Measurements

The electrodes were contacted by probes on the contact pads in two different ways. The silicon chips were either completely immersed in the electrolyte solution and the manipulator tips were replaced by gold wires, or a droplet of the electrolyte was put on the chip covering only the electrodes (to prevent the droplet from running over the contact pads, a rim of silicon grease was made) and the normal manipulator tips were used.

To operate the microactuators, a triangular voltage wave (cyclic voltammetry) was applied to the working electrode/microactuator using an Eco Chemie potentiostat. We used a voltage from 0 to -1 V versus the Ag/AgCl quasi-reference electrode on-chip, with a scan rate of 100 mV/s. We call the on-chip Ag/AgCl reference electrode

a quasi-reference because there are no Cl^- ions in the solution as is the case for a real reference electrode. After a few initial cycles, the microactuators released themselves from the substrate.

Results and discussion

A photograph of a chip with the three electrodes is shown in Figure 4. In this case the sample was completely immersed in the liquid. The total length of the actuator was $70\ \mu\text{m}$, of which $20\ \mu\text{m}$ was attached to the surface. It is bent 90 degrees in the second photo. The speed of the actuators with all the electrodes on-chip was the same as our normal devices, which use large counter and reference electrodes.

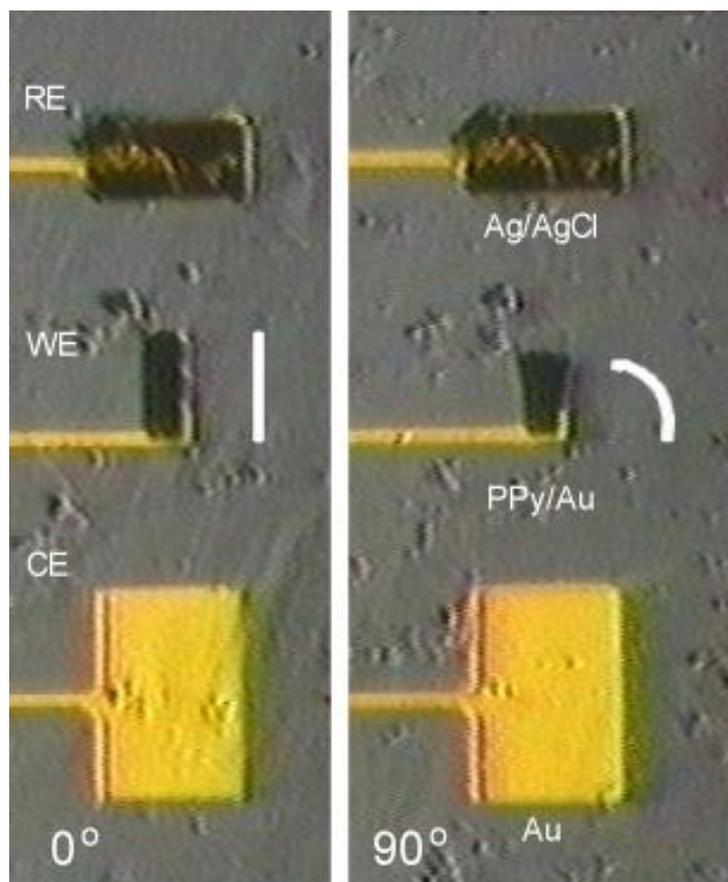


Figure 4 A photograph of the three microelectrodes in an electrolyte solution. The top electrode is the Ag/AgCl quasi-reference electrode ($50 \times 100\ \mu\text{m}^2$), the middle electrode is the PPy/Au microactuator or working electrode ($20 \times 70\ \mu\text{m}^2$) and the bottom electrode is the Au counter electrode ($100 \times 150\ \mu\text{m}^2$). On the left the microactuator lies flat on the substrate, and on the right it is bent perpendicular to the substrate (90°).

Figure 5 shows the cyclic voltammogram (CV) of a sample when connected with normal probe tips and only a droplet of electrolyte covering the electrodes. (The CVs of the completely immersed samples do not give good information because the redox signals are drowned in the residual currents due to the large surface area of the contact pads and gold probe wires compared to the microactuator surface.) A noise signal was to be seen superimposed on the redox currents. (We think that the noise is from a 50 Hz power line and is coupled through the probes. We have also made microelectrodes with non-moving PPy working electrodes. They were contacted with crocodile clips and did not show any noise at the same current levels.) We could remove most of the noise using a smoothing function based on an

FFT algorithm, supplied with the electrochemistry software (Autolab GPES), with a cut-off frequency below the noise frequency peak. The use of the algorithm results in a better signal, as we are used to seeing.

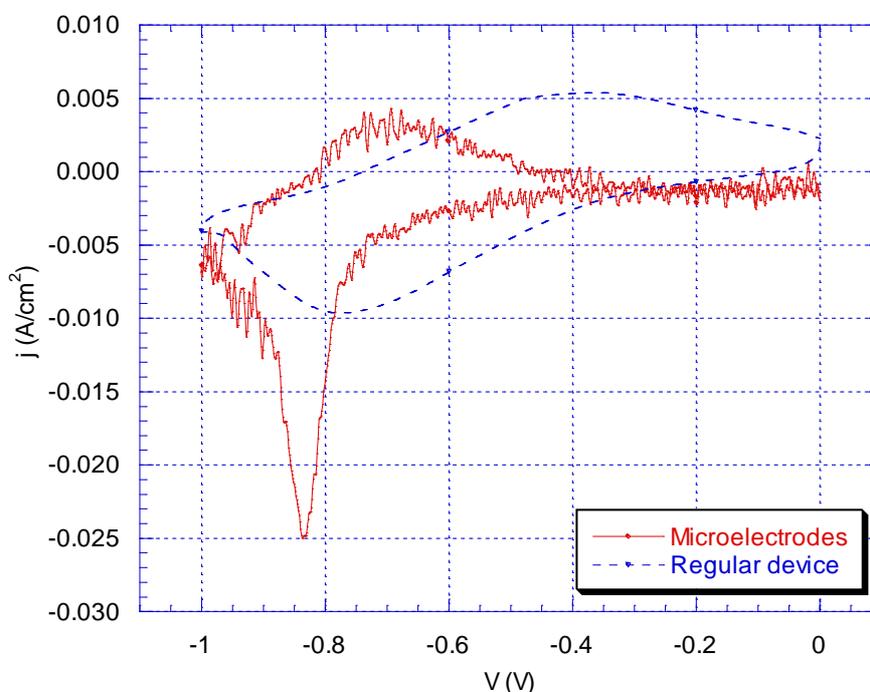


Figure 5 The cyclic voltammogram of one microactuator with all electrodes on-chip compared with the CV of a regular device. This regular device had over a thousand microactuators and used a large CE and RE. The scan rate was 100 mV/s in both cases.

Figure 5 also gives a comparison between the CVs of the device with all electrodes on-chip and a more traditional device. The latter had over a thousand microactuators and used a large CE (Au wire) and Ag/AgCl RE. In both cases the third scan is shown. The reduction ($V \approx -0.85V$) and oxidation ($V \approx -0.7V$) peaks are clearly visible. We can see two differences in the CV of the microelectrodes. First, the oxidation and reduction peaks are shifted cathodically. The oxidation peak is shifted by $-0.3 V$ and the reduction peak by $-0.1 V$. Reasons for this difference could be a voltage drop over the probe tip-contact pad interface and/or the potential of the quasi reference electrode is not well defined. Second, the reduction peak in the microelectrode case is much sharper than the regular one. This distinctly different CV from the microelectrode is interesting from the point of view of the electrochemical properties of polypyrrole, but will not be addressed here.

Now that we have managed to put all the electrodes on-chip, we will try to use these microactuators for cell studies. We want to tap, or make physical contact with, living cells and study their responses to this mechanical stimulation. We have done some preliminary experiments with cells and PPy surfaces, and the use of large counter and reference electrodes has been troublesome under the microscope due to lack of space. Having just a single chip with all the electrodes on it will solve this problem.

The possibility to move the working electrodes out of the chip plane will allow us to go from 2-D to 3-D, here extending just some 50 μm above the chip plane, an altitude freely chosen during the design process. This may be used to disturb the

stagnating fluid layer close to the chip surface, or to move closer to some object to be contacted.

We are also investigating the optimal electrode configuration and ratio of surface areas of the three electrodes. We want to find out which ratio of the areas gives the optimal performance of the microelectrodes/microactuators, and whether the electrode configuration influences their performance. Several micro-electrochemical cells have been presented in the literature [21, 24, 25], but with little evaluation of alternative electrode lay-outs.

Conclusion

We have demonstrated microactuators with all electrodes on-chip, a first step towards an all-polymer system. The microactuators work as well with the miniaturised electrodes on-chip as they do with large, off-chip counter and reference electrodes. The activation speed is similar and we can clearly see a good CV. Noise was present in the CVs, but we did not observe any adverse effects of this noise on the mechanical behaviour. We can therefore now electrochemically control moving microelectrodes to extend from a surface, and thus tap, approach and attach other objects in the electrolyte. Such tools we expect to be useful for single cell studies and for neurophysiology.

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References

- 1 G. Lin, C.-J. Kim, S. Konishi, and H. Fujita, Design, fabrication, and testing of a C-shaped Actuator, *Transducers '95*, Stockholm, Sweden, 1995, pp. 416-419
- 2 T. Ebefors, E. Kalvesten, and G. Stemme, Dynamic actuation of polyimide V-grooves joints by electrical heating, *Euroensors XI*, Warschaw, Poland, Sept 21-24, 1997, pp. 1579-1582
- 3 C. Liu, T. Tsao, Y.-C. Tai, and C.-M. Ho, Surface Micromachined magnetic actuators, *IEEE Workshop on Micro Electro Mechanical Systems*, Oiso, Japan, 1994, pp. 57-62
- 4 C. W. Storum, D. A. Borkholder, V. Westerlind, J. W. Suh, N. I. Maluf, and G. T. A. Kovacs, Flexible, dry-released process for aluminum electrostatic actuators, *J. Microelectromech. Syst.*, 3 (1994) 90-96
- 5 E. Smela, O. Inganäs, and I. Lundström, Controlled folding of micrometer-size structures, *Science*, 268 (1995) 1735-1738
- 6 E. Smela, Microfabrication of PPy microactuators and other conjugated polymer devices, accepted for publication in *J. Micromech. Microeng.*, (1998)
- 7 W. R. Salaneck, I. Lundström, and B. Rånby (eds.), *Conjugated Polymers and Related Materials: The interconnection of Chemical and Electronic Structure*, Oxford Science Publications, Oxford, 1993 ,
- 8 J. C. Gustafsson, B. Liedberg, and O. Inganäs, In situ spectroscopic investigations of electrochromism and ion transport in poly(3,4-ethylenedioxythiophene) electrode in a solid state electrochemical cell, *Solid State Ionics*, 69 (1994) 145-152

- 9 Q. Pei and O. Inganäs, Electrochemical applications of the bending beam method. 1. Mass transport and volume changes in polypyrrole during redox, *J. Phys. Chem.*, 96 (1992) 10507-10514
- 10 Q. Pei and O. Inganäs, Electrochemical muscles: bending strips built from conjugated polymers, *Synth. Met.*, 55-57 (1993) 3718-3723
- 11 R. H. Baughman, Conducting polymer artificial muscles, *Synth. Met.*, 78 (1996) 339-353
- 12 T. F. Otero and J. M. Sansinena, Artificial muscles based on conducting polymers, *Bioelectrochemistry and Bioenergetics*, 38 (1995) 411-414
- 13 A. Della Santa, D. De Rossi, and A. Mazzoldi, Characterization and modelling of a conducting polymer muscle-like linear actuator, *Smart Mater. Struct.*, 6 (1997) 23-24
- 14 A. P. Lee, K. C. Hong, J. Trevino, and M. A. Northrop, Thin film conductive polymer for microactuator and micromuscle applications, *Dynamic and Systems and Control Session, International Mechanical Engineering Congress, Chicago, USA, 1994*, pp. 725-732
- 15 R. M. Torresi, S. I. Cordoba de Torresi, T. Matencio, and M.-A. De Paoli, Ionic exchanges in dodecylbenzenesulfonate doped polypyrrole, Part II: Electrochemical quartz crystal microbalance study, *Synth. Met.*, 72 (1995) 283-287
- 16 J. F. Rusling and S. L. Suib, Characterizing materials with cyclic voltammetry, *Adv. Mater.*, 6 (1994) 922-930
- 17 J. Heinze and M. Dietrich, Cyclic voltammetry as a tool for characterizing conducting polymers, *Materials Science Forum*, 42 (1989) 63-78
- 18 J. M. Sansiñena, V. Olazabal, T. F. Otero, C. N. Polo da Fonseca, and M.-A. De Paoli, A solid state artificial muscle based on polypyrrole and a solid polymeric electrolyte working in air., *Chem. Commun.*, (1997) 2217-2218
- 19 T. W. Lewis, G. M. Spinks, G. G. Wallace, D. D. Rossi, and M. Pachetti, Development an all polymer electromechanical actuators, *Polymer Reprints*, 38 (1997) 520-521
- 20 T. F. Otero, personal communication
- 21 P. Arqint, Integrated blood gas sensor for pO₂ pCO₂ and pH based on silicon technology, PhD thesis, Institute of Microtechnology, University of Neuchâtel, 1994
- 22 E. Smela, O. Inganäs, and I. Lundström, Differential adhesion method for microstructure release: an alternative to the sacrificial layer, *Transducers '95, Stockholm, Sweden, 1995*, pp. 218-219
- 23 F. A. Lowenheim, *Electroplating*, McGraw-Hill, New York, 1978, pp. 257-263
- 24 G. D. T. Bratten, P. H. Cobbold, and J. M. Cooper, Micromachining sensors for electrochemical measurement in subnanoliter volumes, *Anal. Chem.*, 69 (1997) 253-258
- 25 H. Suzuki, A. Sugama, and N. Kojima, Micromachined Clark oxygen electrode, *Sensors and Actuators B*, 10 (1993) 91-98