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A preliminary study of conducting polymers as microvalve seals

Q. Fang^{a,b,*}, D.G. Chetwynd^a, J.W. Gardner^a, C. Toh^{c,1}, P.N. Bartlett^c^a School of Engineering, University of Warwick, Coventry CV4 7AL, UK^b Institute of Solid State Physics, Chinese Academy of Science, Hefei 230031, People's Republic of China^c Department of Chemistry, Southampton University, Southampton SO17 1BJ, UK

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Abstract

We report here on the first investigation into the behaviour of conducting polymers as seals for microvalves. Poly(pyrrole) is known to be reasonably stable in air and is also one of the easiest conducting polymers to synthesise either by chemical or electrochemical polymerisation. It is known to offer interesting tribological properties and so is chosen as the exemplar material here. Poly(pyrrole) with three dopants, namely 1-decanesulfonate (DSA), methylphosphonate (MPA) and 1-butanedisulfonate (BSA) films were deposited electrochemically with a thickness between 0.5 and 1.5 μm , on gold electrodes patterned on Si-wafer (4×4 mm). Test results show that the leakage rate for the PPY films can be down to $0.5 \text{ cm}^3 \text{ min}^{-1}$. The PPY films doped with MPA have the best performance. The effects of the choice of the electrochemical deposition conditions and resulting morphology, the film thickness and the choice of counter-ions on the leakage rate are also discussed.

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1. Introduction

Molecular electronic materials, including organic, polymeric or even biological materials, can offer viable alternatives to traditional materials in many applications. Conductive polymers have attracted a lot of interest in a wide range of applications from electronic displays and solar cells to sensors and actuators in microengineering and nanotechnology due to their excellent physical properties, ease of fabrication and low cost. This has led to some serious attempts at exploiting them for mechanical and tribological applications [1,2]. Poly(pyrrole) is one of the most promising candidates for use as an active component in many technological applications such as solar cells, sensors and actuators [3–6]. The microstructures and mechan-

ical properties of conducting polymers are critically important for many of their applications. We have previously investigated the friction and tensile strength of poly(pyrrole) films. There is strong evidence that the film morphology and film thickness play an important role in their mechanical and tribological properties [3,7]. The conducting polymer thin films can be fabricated by processes compatible with microelectronic and micro-mechanical technologies but the properties of these polymers are very different to those of materials traditionally used. For example, their compliance and sealing properties could be advantageous in making micro valves and micro pumps for fluidic chips or even in Lab-on-a-chip applications. Here we report the results of the first, preliminary investigation into the behaviour of conducting polymers as seals for microvalves in order to establish a rationale for a more detailed study. Poly(pyrrole) is known to be reasonably stable in air and is also one of the easiest to synthesise either by chemical or by electrochemical polymerisation [8,9]. The research seeks to improve understanding of materials, mechanics, electrochemistry and microfabrication. Further, it may provide tools to improve the effectiveness of microsystems to the benefit of, for

* Corresponding author. Present address: Department of Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, UK. Tel.: +44-20-7679-3196; fax: +44-20-7388-9325.

E-mail address: q.fang@ee.ucl.ac.uk (Q. Fang).

¹ Present address: Division of Chemistry and Chemical Engineering, California Institute of Technology, USA.

example, instrumentation, speciality fine chemical production, and bio-medical systems.

2. Experimental details

2.1. Fabrication of O-ring and polymer growth

There are several established methods for depositing thin films of PPY, but the work reported here uses only direct electro-deposition from solution. Fabrication of polymer O-rings involves two stages, namely photolithographic patterning of an electrode (usually platinum or gold) and electrochemical deposition of the polymer. The O-ring mask design was produced using the software package L-EDIT (Tanner Tools). Four inch Si-wafers were processed by first growing 800 nm of thermal oxide, followed by LPCVD of 150 nm of silicon nitride. A complete layer of electrode material was comprised of 185 nm of platinum including a thin tantalum seeding layer. Next a 200 nm layer of PECVD nitride was patterned to define the platinum O-rings and wire-bond pads. The wafer was diced to produce 4 mm² dies each containing one O-ring. To electrochemically produce a PPY thin film, the pyrrole monomer (freshly purified by distillation or by filtration using ultra fine Al₂O₃ (size < 1.0 μm)) was dissolved in water, with a suitable electrolyte containing the chosen counterion. All depositions were carried out in a standard three-electrode electrochemical cell (see Fig. 1). Three electrolytes were used in the present investigation; DSA (sodium 1-decanesulfonate, 98% Aldrich), BSA (sodium 1-butananesulfonate, 98% Aldrich) and methylphosphonic acid (MPA, 98% Aldrich).

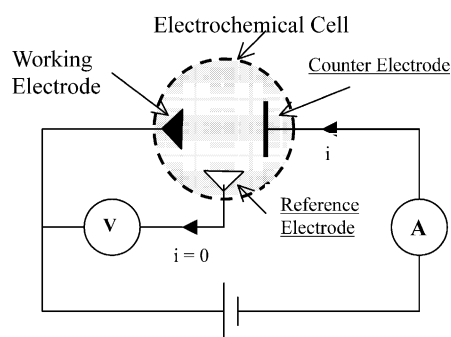


Fig. 1. Schematic of a standard three-electrode electrochemical cell.

Three nominal thicknesses of poly(pyrrole) O-ring were deposited onto each of three sizes of electrode, as specified in Table 1. The films were deposited from a 0.1 mol dm⁻³ solution of pyrrole containing 0.1 mol dm⁻³ concentration of the electrolyte, which provides the counter anion in the polymer film. Electropolymerisation was carried out potentiostatically with a maximum potential between 0.5 and 0.9 V (these potentials were chosen at values just above the polymerisation potentials of pyrrole in the presence of the different electrolytes. This is to study the effect of polymerisation rates on the morphologies and seal properties of the polypyrrole films) with respect to a home-made standard calomel electrode (SCE) reference. The thickness of the film was estimated from the total charge passed. In order to ensure uniform and good adhesion of PPY films grown on the Si-wafer, the Pt electrode was cleaned electrochemically prior to polymer deposition. This process involved cycling the Pt electrode potential several times between -0.2 and +1.2 V at a sweep rate 100 mV s⁻¹ in 2 M sulphuric acid. Full details of the electrochemistry may be found elsewhere [10–12]. Fig. 2 shows both an optical micrograph of a typical uncoated O-ring specimen defined by a window through nitride to gold on a Si substrate (SRL168) and an interferometric view of a typical polymer coated specimen. Fig. 3 shows a schematic of the test arrangement; it also illustrates how it might typically be used as a microvalve to maintain a partial vacuum against ambient atmosphere.

2.2. Testing of leakage rates

In order to gain basic information on the behaviour of the PPY O-rings, a very simple vacuum test rig (Fig. 3) has been designed to determine their sealing properties for air at moderate pressure differentials. The microvalve test rig consists of a stainless steel container (25 ml in volume), a vacuum system and a digital pressure transducer. The O-ring was rested on a horizontal smooth glass surface, completely surrounding a 0.7 mm hole, and the container partially evacuated. The pressure difference across the O-ring die provides a compressive force on the ring, as in a 'self-actuating' valve. The valves were then closed and the pressure in the container monitored over time as air leaked in via the O-ring seal. For this preliminary study, data were recorded manually. The test pressure in the canister

Table 1
Various designs of polymer O-rings for experimental testing

SRL number	Diameter (outer) (μm)	Diameter (inner) (μm)	Thickness (μm)
166	1450	1750	0.5, 1.0, 1.5
167	1450	1650	0.5, 1.0, 1.5
168	1450	1550	0.5, 1.0, 1.5

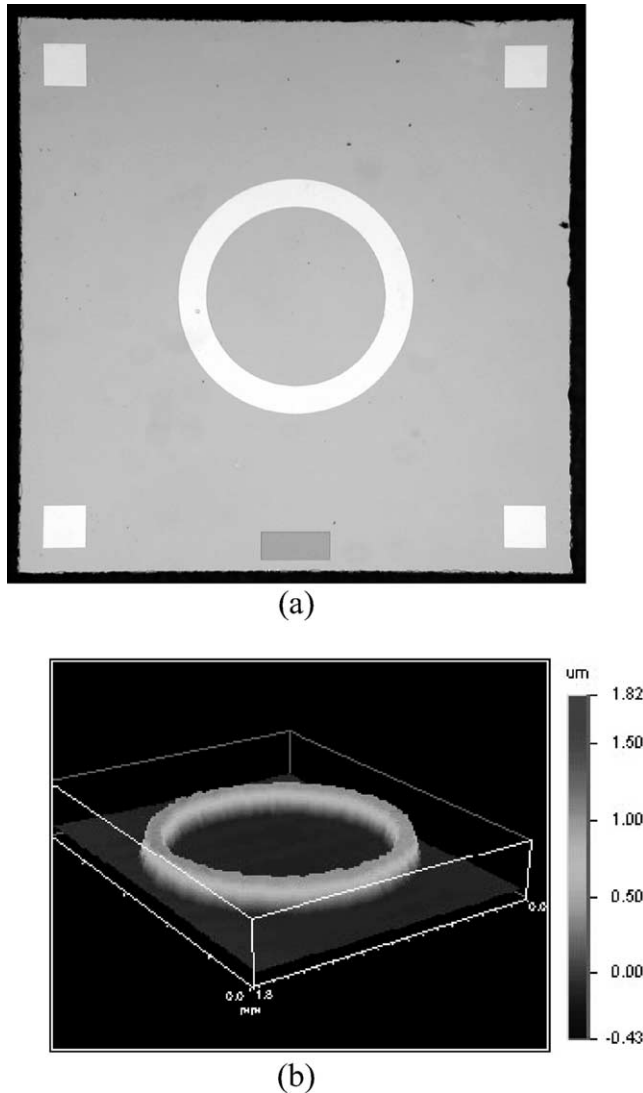


Fig. 2. (a) Optical micrograph of O-ring substrate (SRL168), (b) scanning interferometer view of a polymer O-ring. The mean diameter of the ring is 1500 μm .

(absolute) for this work ranges from 10^{-2} to 90 kPa. In each case measurements were made on at least three replicate samples deposited under identical conditions in

order to confirm the reproducibility of the behaviour between polymer samples.

3. Results and discussion

3.1. Measurement of leakage rate

Fig. 4 shows typical leakage behaviour, from a PPY ring with a 2 μm thick layer. Initially, the container is at very low pressure and almost full atmospheric pressure (about 100 kPa) occurs across the chip and seal. The force pressing the seal onto the glass counterface arises from this pressure difference acting over the area inside the ring (neglecting extra effects from within the ring itself). As air leaks into the container, the internal pressure rises as shown in Fig. 4(a). Taking air as a perfect gas, the absolute pressure (together with the fixed volume and temperature) allows the mass of air within the container to be estimated, and so the mass flow rate can be found. The mass flow is converted to an equivalent volume flow at atmospheric pressure, Fig. 4(b), as being more representative of a design parameter for a real microvalve.

The leakage rate is initially high since there is a large pressure difference across the seal. The relatively high resultant flow rate causes a rapid rise in internal pressure, leading to a reduced pressure differential and a reducing flow rate. The force pressing the ring onto the counterface reduces over time, which is likely to increase the leakage somewhat, but in practice the effect appears to be secondary. The example in Fig. 4 shows a rather high initial flow of around 5 ml min^{-1} , dropping to 1 ml min^{-1} after 7 min. The behaviour is close to that of a first-order system, so time sequences are retained as a means of comparing data sets. As verification of the integrity of the equipment, the same test was run with a conventional rubber O-ring and a flat glass cover. The leakage was then only 20 $\mu\text{l min}^{-1}$ even though a high-pressure difference was maintained over the period of the test. Morphology and microstructure of the PPY are

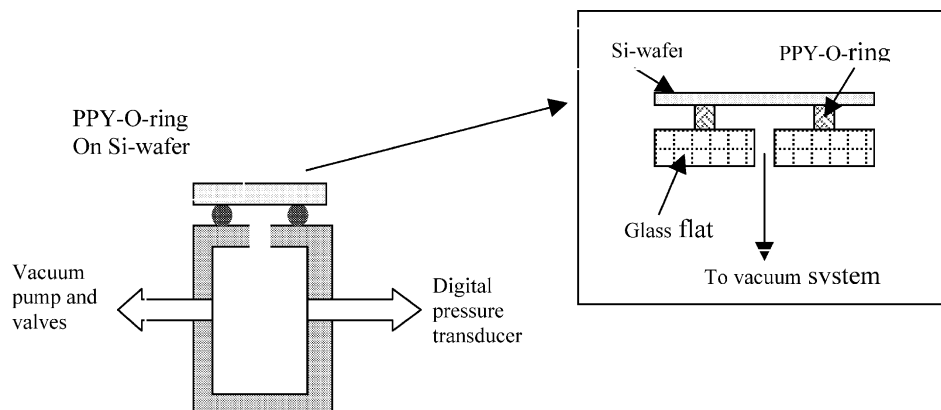


Fig. 3. Basic schematic of the micro-valve testing rig.

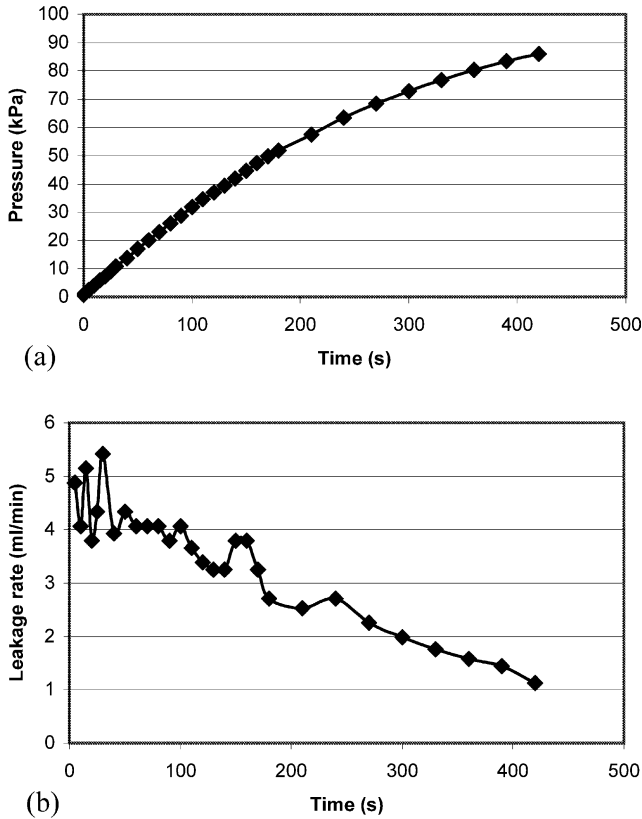


Fig. 4. Leakage behaviour over time of a typical test on sample 166-1. (a) Shows a pressure change within the test volume (b) is the derived leakage rate against test time.

likely to be important factors contributing to the leakage and were further explored.

The polymer ring seal samples were obtained under different polymerisation potentials in order to study the best condition for obtaining smooth polymer morphology and at different polymerisation times to obtain different polymer thicknesses. It is difficult to control the polymer thickness due to the rapid polymerisation process ~ 3 to 15 s and the variation of polymerisation

Table 2
WYKO measurement data from PPY(DSA)-O-rings on Si-wafer

Sample number	Thickness (μm)	R_a (nm)
166-1	2.01	85.48
166-2	0.92	14.56
166-3	0.5–0.6	1.75
167-1	1.25	23.46
167-2	0.7–0.85	4.16
167-3	0.55	0.89
168-1	1.52	30.52
168-2	1.10–1.15	23.02
168-3	0.60–0.62	1.51

rates even when the experimental conditions were identical. It is, therefore, difficult to compare identical films due to this variation in the polymerisation rates. We can however, make many samples under the same polymerisation conditions and use only those with the same thickness. This is the case for Figs. 7 and 8 in this paper.

3.2. Morphological and effect of thickness of PPY films on the leakage rate

Atomic force microscopy, scanning electron microscopy, surface topographic measurement (WYKO NT2000) and optical microscopy were used to characterise the films before and after testing. Table 2 shows the WYKO measurement data from the PPY-O-rings, doped by DSA. The results demonstrate that the surface average roughness R_a increases sharply with the increasing thickness of PPY films (Fig. 5). Fig. 6 shows the effect on leakage rate of the thickness of the PPY film for the narrow and wide rings. Leakage clearly increases with film thickness. Since surface roughness increases with thickness (Fig. 5), it is not clear whether the internal morphology or the topography of the film plays a dominant role. Probably, both parameters have

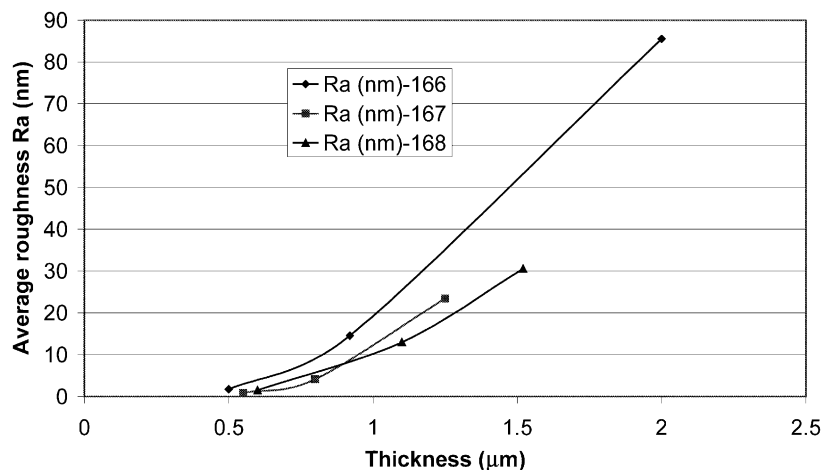


Fig. 5. Surface average roughness R_a of PPY O-rings SRL 166, 167 and 168 with different seal thickness.

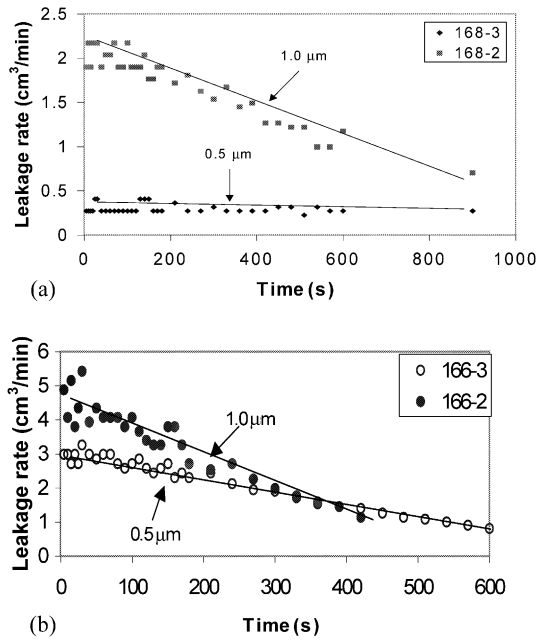


Fig. 6. Effect of thickness of polymer O-ring films on gas leakage rate for PPY O-rings types SRL 166 (a) and 168 (b).

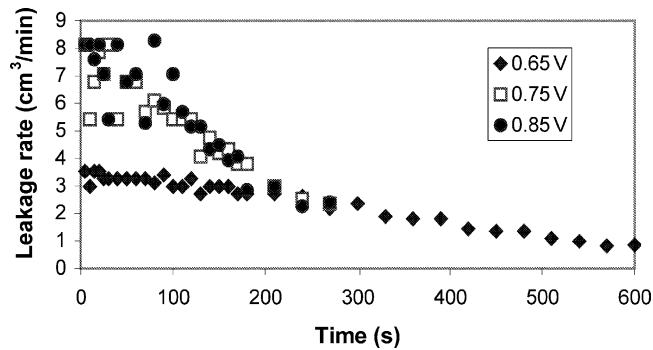


Fig. 7. Leakage rate of thin PPY/DSA O-rings deposited with different cell-potentials, film thickness of $2.1 \pm 0.3 \mu\text{m}$.

significant effect on leakage, but a larger, more detailed study is needed to resolve this issue.

3.3. Effect of potential used in the electrochemical deposition on leakage rate

Many factors can influence the morphology and microstructure of PPY thin films in electrochemical processing. The potential used in the electrochemical cell controls the deposition rate and growth dynamics, which may change the surface morphology and microstructure. Fig. 7 shows the leakage rate of PPY/DSA thin films (film thickness $2.1 \pm 0.3 \mu\text{m}$) deposited at different potentials. O-rings grown at 0.65 V versus SCE had the lowest initial leakage rate of about 3 ml min^{-1} . Leakage was higher for polymer(s) deposited at 0.75 V, and increases again for polymer(s) deposited at 0.80 V

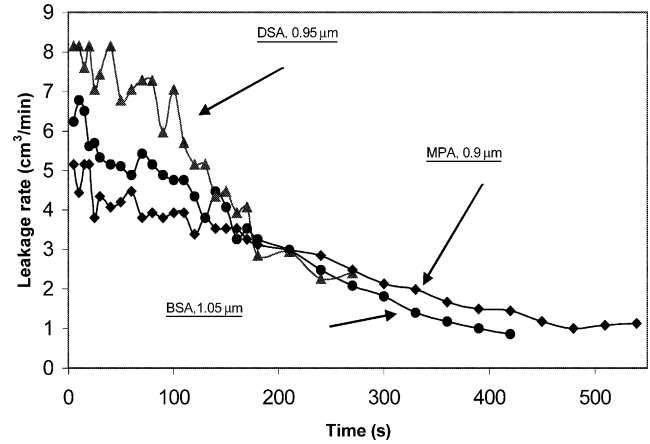


Fig. 8. Leakage rate of PPY thin films deposited using different counterions.

and then at 0.85 V showed no further significant increase of leakage rate. Lower cell-potentials led to slower deposition rates, which can produce smoother surfaces and denser, more uniform structures in the PPY thin film.

3.4. Effect of the counter-ions incorporated in the PPY film on the leakage rate

Fig. 8 shows leakage rates of PPY thin films deposited using different counter-ions. The initial leakage rate was lowest with the MPA counter-ion, higher with BSA and higher again with DSA. This order correlates with increasing length of the alkane chain and thus overall size and hydrophobicity of, the counter-ion. Fig. 9 shows the surface morphologies of PPY/BSA and PPY/MPA films (both deposited at 0.85 V, and 1 μm thick). The surface of PPY/MPA film is smoother, R_a roughness 2.7 nm, than that of PPY/BSA film, R_a about 28 nm. Once again, the results of the measurements are consistent with the view that the morphological and microstructure properties on the surface of the polymer O-ring are critical to the gas seal quality.

It should be noted that all the tests described here were performed on 'new' rings. Some films were observed to be rather fragile. It is, therefore, quite possible those film properties vary with repeated use and that endurance to repeated use might depend on the film type. A larger, focussed study is being planned that will include such questions.

4. Conclusions

We report on the initial investigation of the deposition and microstructures of conducting polymers as seals for microvalves. Morphological and microstructural properties on the surface of the poly(pyrrole)

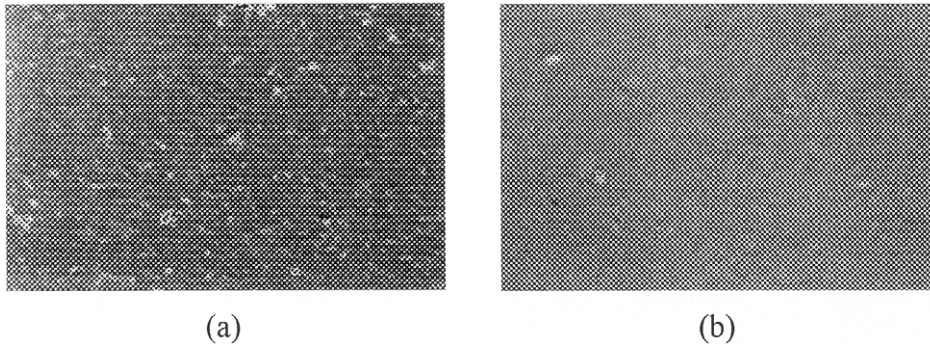


Fig. 9. Surface topographies of (a) PPY/BSA ($R_a = 28.12$ nm) and (b) PPY/MPA ($R_a = 2.70$ nm), film thickness of 1 μm , grown at 0.85 V.

micro-O-rings appear critical to our understanding of leakage mechanisms and to improving the seal quality of conducting polymers. A larger study is now starting, informed by the following observations.

Thicker PPY O-ring films have bigger surface roughness, and a bigger leakage rate during the test.

The potential used in the electrochemical cell can control the deposition rate, the surface morphology and microstructure of PPY thin films. Lower cell-potential led to a slower deposition rate, which can produce a smoother surface morphology, and a lower leakage rate.

The leakage rate of PPY thin films with MPA counter-ions was lower than with BSA and DSA counter-ions.

Simple tests on PPY O-rings as hermetic seals are promising and suggest that their sealing properties for liquids would be excellent. The application of polymer seals in the assembly of microfluidic and bioMEMS devices appears plausible and further study is recommended.

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