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Combined chemical and electrochemical synthesis methods for metal-free polypyrrole actuators.

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Abstract

Novel combined chemical-electrochemical synthesis routes for the preparation of metal-free air-operated polypyrrole-based actuators are presented. The chemical synthesis phase provides the conductive electrode surface for the well-controllable electrochemical deposition of the working PPy material. Several new techniques not previously used in conducting polymer actuator preparation are described, including vapor-polymerization, oxidizer-painting and low temperature electrosynthesis in mixed aqueous solutions. Both commercially available and in-house membranes were used. The three described methods yielded well reproducible, functional actuators with acceptable displacement, strains and strain-rates. The most important characteristics of the actuators are presented.

Keywords: electroactive polymers, polypyrrole, actuators, air-operated, chemical synthesis, electrochemical synthesis

1. Introduction

Electromechanically active materials are materials that change their shape under applied potential or generate electrical signal upon mechanical stimulus. Among the various material candidates, both ionic and non-ionic electroactive polymers (EAP) have recently drawn much attention. This kind of soft, lightweight actuators can undergo a significant amount of deformation while sustaining relatively large forces, and can be used for constructing actuators, sensors or energy harvesting devices. Compared to conventional electromechanical counterparts, actuators made from such novel and advantageous materials are: easily miniaturized, soft, light-weight, have simple mechanics, good force-to-weight ratio, and inherent vibration damping. Some fields of applications that have either been proposed or are already being developed include micro-actuators [1], bio-mimetic manipulators [2,3], space [4-7], and medical applications [8].

Conducting polymer (CP) based actuators date back to about 20 years [9,10]. They have some important advantages over other traditional EAP materials, like ionic-polymer-metal composites, such as larger maximum forces, inherent conductivity, catch-states, virtually endlessly tunable properties (due to their electrochemical synthesis), biocompatibility in case of polypyrrole (PPy), for instance. Polyaniline, PPy, and poly(3,4-ethylenedioxythiophene) (PEDOT) are perhaps the most common representatives of CPs. Some of the shortcomings of CPs as electromechanically active materials are related to the delamination from electrodes (and loss of contact), overly high stiffness, slow response, requirements on environment, stability (especially of those used in biological environments, aqueous solutions and/or in air [11-13]) etc. Most efforts up-to-date have been focused on bending-type motion; some important milestones in the progress of their research include single layer actuators [14], use of lowered synthesis temperatures [15,16], use of ionic liquids (ILs) instead of aqueous solutions [17], and perhaps most importantly – by creating various composites [18-20], including semi inter-penetrated networks (IPN) [21,22]. The IPNs and other membrane based
constructions have finally offered at least partial solution to one of the main drawbacks of CP based layered actuators – delamination – while at the same time providing storage for the mobile species, enabling the use of the actuators without the surrounding media having to act as an ion reservoir.

One of the common problems with creating actuators around such membranes lies in the fact that the electrochemical deposition of the CP material requires an electrode, hence, the surfaces of the membrane have to be made conductive. The electrochemical deposition is favored because of the obtainable quality of the films and the much better control over the process. Initial attempts were focused on the separate electrosynthesis of the CP layers followed by attaching these to the membrane [23]. Unfortunately the advantage of simplicity is outbalanced by delamination. The other obvious approach is to use some form of metal coating, like sputtering [24-26] or vacuum evaporation [27,28] of some noble metal. However, there is also the option to use chemical polymerization of the same CP into the membrane as the means for creating a conductive surface. The advantages over metal coating are the abatement of the delamination risk and avoiding the cost/cumbersomeness of vacuum techniques. To our best knowledge, the only attempt to use chemically deposited CP as the electrode material for the following electrochemical deposition onto a membrane material has been made with PEDOT into nitrile butadiene rubber [29] for non-actuator purposes. The choice of the membrane material is paramount. In case of some CPs (like PEDOT) the secondary role of the membrane is to increase rigidity; in case of PPy, which is rigid enough, the membrane should rather introduce elasticity. The pore size of the membrane must also be considered. Optimal pore size would allow the CP to penetrate deep enough to have strong adhesion while not too deep to cause short-circuits. The total pore volume has to be sufficient to contain the mobile species. Poly-1,1-difluoroethene (polyvinylidene fluoride), (PVdF) is often used as a membrane for PPy-based actuators, as it is known to be a soft, flexible and porous material.

In the present study, several possibilities of obtaining metal-free actuators by depositing PPy chemically into the surface of the membrane followed by the electrochemical synthesis were investigated. PVdF-related membranes, both in commercial and in-house flavors, and two different electrolytes: 1-ethyl-3-methylimidazolium tetrafluoroborate and lithium bis(trifluoromethane)-sulfonimide, were used.

2. Experimental

2.1. Materials

Pyrrrole (Py, Sigma-Aldrich) was purified by distillation over calcium hydride under vacuum and stored in the dark under Ar atmosphere at low temperature. 4-Methyl-1,3-dioxolan-2-one (propylene carbonate, PC, Fluka), sodium 2-dodecylbenzenesulfonate (NaDBS, Sigma-Aldrich), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄, Sigma-Aldrich), lithium bis(trifluoromethane)-sulfonimide (LiTFSI, Sigma-Aldrich), poly(vinylidene fluoride-co-hexafluoropropene) (PVdF-HFP, average molecular weight $M_w = 130000$, Fluka), 4-methylpentan-2-one (MP, Fluka), ethan-1,2-diol (monoethylene glycol, MEG, AS Keemiakaubandus), disodium sulfonatoxy sulfate (Na₂S₂O₈, AG Chemia), iron trichloride (FeCl₃, AG Chemia), 3-methylphenol (m-Cresol, Sigma-Aldrich) were used as received. Ultra pure MilliQ+ water was used. All solutions were degassed in ultrasonic bath before use.
2.2. Membranes

Two different membrane types were used for comparison: commercial Millipore Immobilon-P (according to product specification: hydrophobic, thickness 125 µm, pore size 0.45 µm), porosity 70%, and in-house solid gel membrane prepared similarly to the procedure of Sugino et al [30].

Solid gel membrane was prepared from 200 mg (8 wt.%) EMIBF₄ and 200 mg (8 wt.%) PVdF-HFP dissolved in a mixture of 2 ml (64 wt.%) MP and 500 mg (20 wt.%) PC. This mixture was heated to 70 °C and stirred on a magnetic stirrer overnight. The mixture was poured into the 50 × 50 mm polytetrafluoroethylene (PTFE) mold (initial thickness, estimated from volumes of compounds was 1.07 mm). Solid membrane film was obtained after the solvent (MP) evaporated. Membrane porosity, estimated as electrolyte volume (EMIBF₄ in PC) ratio to total membrane volume after solvent (MP) evaporation was 83%. Membrane thickness, calculated from the electrolyte and PVdF-HFP volumes was 273 µm and the thickness, as estimated from SEM micrographs before swelling in target electrolyte, was 140 µm. Differences can be explained by the temporary collapse of the membrane skeleton due to the evaporation of PC in air or in vacuum during the scanning electron microscopy, and/or electrolyte diffusion out of the membrane during the following electrochemical synthesis procedure.

2.3. Chemical synthesis

Several attempted alternative techniques for creating a conductive layer on the membrane are summarized in Table 1. Three different methods for the chemical synthesis step with the most reproducible results were used for the preparation of the characterized actuator materials. For both immersion methods, Na₂S₂O₈ as the oxidant instead of the commonly used FeCl₃ was chosen in order to avoid the formation of insoluble iron complexes with DBS [31].

2.3.1. Millipore Immobilon-P membrane, immersion method (MPI-immersion)

Commercial PVdF membrane was permeated with Py monomer and immersed in 0.044 M Py, 0.015 M NaDBS, and 0.1 M Na₂S₂O₈ aqueous solution at 70 °C for 20 seconds; the polymerizing Py from outer-most pores turned the membrane black. Elevated synthesis temperature was chosen to increase the polymerization rate (decrease polymerization time) to avoid short circuits between electrodes caused by too deep oxidant penetration into membrane. Chemical synthesis was terminated by washing membrane with cold methanol.

2.3.2. Millipore Immobilon-P membrane, vapor phase synthesis method (MPI-vapor)

Synthesis principle for the chemical phase is similar to that of Lei et al [32]. PVdF membrane permeated with 0.5 M FeCl₃ solution in PC, swept with filter paper and exposed on glass plate between two Petri dishes to Py vapors at 40 °C until the membrane turned black (about 15 minutes). After flipping around, the membrane was swept clean again and the exposure was repeated for the other side. The resulting membrane was then thoroughly rinsed with methanol.

2.3.3. In-house electrolyte membrane, immersion method (IH-immersion)
Chemical synthesis of PPy on in-house solid gel membrane was carried out at room temperature (22 ± 2 °C). Membrane previously cooled down to -30 °C to reduce diffusion between membrane and solution was immersed in 0.044 M Py, 0.015 M NaDBS, and 0.1 M Na2S2O8 aqueous solution for 200 seconds under gentle agitation; the membrane surface turned black as the PPy deposited. The membrane was then washed with water between fingers to remove the detached remains of PPy deposit. Finally, the chemically coated membrane was dried in air for 30 minutes.

2.4. Electrochemical synthesis

Electrochemical synthesis of PPy, done in the same way for all membranes, was carried out galvanostatically (controlled by PARSTAT 2273) in a one-compartment two-electrode electrochemical cell at current density 0.1 mA·cm⁻² and temperature -23 ± 2 °C until total charge 2 (MPI-vapor), 4 (IH-immersion) or 8 C·cm⁻² (MPI-immersion) was consumed. PPy was deposited on both sides of 30 × 30 mm membrane sheets using the chemically synthesized PPy coating as the conducting anode, and symmetrically placed stainless steel (AISI 316L) mesh sheets as cathodes. The synthesis solution contained 0.2 M Py and 0.2 M NaDBS dissolved in a mix of water and MEG (1:1 vol.%). DBS⁻ as doping anion, low synthesis temperature and low current density were chosen for the good mechanical properties [33] and improved actuation properties [34] of the resulting PPy actuator. The relatively large doping anion was chosen to enforce cation movement during redox cycles, and quick recovery of the conductivity upon oxidation after the reduction half-cycle. Water and MEG mix was chosen because of good solubility of NaDBS in water, low freezing point (-34 °C) and for the plasticizing properties of MEG.

Relatively low synthesis potential at the initial stage of the synthesis suggests the polymerization of the adsorbed monomer layer. Higher potential for stainless steel electrode is related to the higher polymerization potential of PPy on stainless steel, as compared with the synthesis onto an existing PPy layer. Initial potential rise is caused by the evolution of the monomer concentration gradient (Fig. 1 A-B, first 10000 seconds) and decreasing surface area (Fig. 1 A, the electrochemically synthesized layer is much smoother than the thin chemically synthesized layer on the porous membrane surface. See also Fig. 2 D). In case of the chemically synthesized base layer (Fig. 1 A) those effects are partially compensated by the improved conductivity of the electrochemically synthesized PPy.

The resulting actuator material was very smooth and flexible, easily cut using scalpel or scissors. Each actuator material sheet was cut into 3 × 20 mm strips using paper guillotine. Actuator width was chosen according to Minato et al [24] in order to minimize curling along actuator length in PC solutions.

2.5. Electrolytes

Several electrolytes were compared in the combinations of different membranes and preparation methods. Due to the preparation method, exchange of the electrolyte was more difficult for in-house solid gel membranes. Electrolyte was added/exchanged with 1 hour of low power ultrasonication followed by 48 hours soaking in target electrolyte. The following electrolytes were used: 1 M EMIBF₄ in PC and 1 M LiTFSI in PC.

2.6. Characterization
Electrical resistance of the chemically synthesized layers and the electrical conductivity of the final electrode layers were measured with a 4-point probe. Electrical conductivities were calculated according to the Smits equation [35]:

$$\sigma = I \cdot (4.532 \cdot w \cdot V)^1$$

where \( \sigma \) is the electrical conductivity, \( w \) is the thickness of the electrochemically synthesized PPy layer as measured from SEM micrograph, \( I \) is the applied constant current between outer contacts of probe, and \( V \) is the measured voltage between inner contacts.

Assuming constant thickness of the actuator and uniform curvature at displacement peak value (using short-enough distance between the fixed end of the actuator and measurement point), strain was calculated according to Sugino et al [30]:

$$\varepsilon = \frac{2 \cdot D \cdot W}{L^2 + D^2}$$

where \( \varepsilon \) is the strain, \( D \) is half of the peak to peak displacement, \( W \) is the thickness of the actuator, measured with micrometer after swelling in target electrolyte, and \( L \) is the distance from the fixed end of the actuator to the projection of the laser beam to plane parallel to the middle position of the actuator. Strain rate is estimated similarly to Madden et al [23] as the average over a full bending cycle (full cycle of applied potential) assuming uniform strain along the actuator:

$$\varepsilon r = \varepsilon \cdot 4 \cdot f$$

where \( \varepsilon \) is the strain, \( f \) is the frequency of applied potential and constant 4 is the number of movements (passages) between neutral and utter position during the full cycle of the applied potential. Scanning electron micrographs were obtained using a Hitachi TM3000 microscope (acceleration voltage 5 kV, back-scattered electron detector). For cross-section images, samples were broken at boiling nitrogen temperature.

Simultaneous measurements of voltage, current, and displacement or blocking force were performed using an in-house setup consisting of a National Instruments PCI-6036E analog input DAQ, laser displacement meter Banner LG10A65PU and isometric force transducer ADInstruments MLT0202.

3. Results and discussion

For brevity’s sake, only the most characteristic results are described for chosen membrane preparation methods and electrolyte combinations.

3.1. Preparation of conducting electrode on a porous membrane

In addition to the three aforementioned chemical synthesis methods, several other techniques were also attempted. Some of them proved to be more suitable for commercial membranes, others for solid gel electrolyte membranes. Qualitative results are summarized in Table 1.

Table 1. Attempted alternative techniques for the preparation of the conducting electrode layer.
<table>
<thead>
<tr>
<th>Method</th>
<th>Membrane type</th>
<th>Millipore Immobilon-P</th>
<th>In-house solid gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pretreatment with graphite powder instead of chemical polymerization.</td>
<td>High electrical resistance, graphite partially detached before electropolymerization, synthesis potential too high under galvanostatic conditions.</td>
<td>Not applicable (lack of adhesion).</td>
<td></td>
</tr>
<tr>
<td>Pretreatment with PPy solution in m-Cresol prepared according to [36].</td>
<td>Satisfactory (low) electrical resistance. Partial detachment of the conducting layer before electropolymerization.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane surface painted with 0.5 M FeCl₃ solution in mix of water and methanol (5:1 vol.%) followed by vapor phase chemical synthesis analogous to method described in Section 2.3.2.</td>
<td>Suitable. Difficult to avoid sporadic short circuits between the sides of the membrane.</td>
<td>Suitable.</td>
<td></td>
</tr>
<tr>
<td>Chemical synthesis for 30 minutes in solution described in Section 2.3.3 at 0 °C; membrane pores were filled with frozen m-Cresol.</td>
<td>Suitable.</td>
<td>Not applicable.</td>
<td></td>
</tr>
<tr>
<td>Immersion method according to Section 2.3.3.</td>
<td>Unsuccessful. Chemical synthesis occurred also inside pores creating short circuits between the sides.</td>
<td>Suitable.</td>
<td></td>
</tr>
</tbody>
</table>

Although all the methods marked as suitable gave generally similar actuators, the three methods described in Section 2.3 exhibited the most reproducible results. Due to the hydrophobicity and large pore size, the main problems with the commercial membranes were obtaining a sufficiently thick PPy layer in outer-most pores while avoiding short-circuits between the sides of the membrane.

3.2. Structure and morphology

The surface of the membranes after the chemical synthesis of PPy by any of the used methods appears relatively rough and porous, following the morphology of the membrane both at nano (Fig. 2 A, C) and micro scale (Fig. 2 B). The micrographs (Fig. 2 A, F) also illustrate the density difference of the two membrane types. The chemically
The electrochemically synthesized layer makes up for most of the PPy mass, and has a much smoother surface (Fig. 2 D). Measurements from SEM micrographs (Fig. 2 E) confirm that the electrochemical synthesis charge density 4 C·cm⁻² (IH-immersion) yields a 25 µm thick PPy layer (according to [37] 160 mC·cm⁻² yields a 1 µm thick coating, indicating that chemically synthesized layer is sufficient to act as a conventional electrode.

### 3.3. Electrical resistance of the base layer and the electrical conductivity of the electrodes

The measured electrical resistances of the chemically synthesized polypyrrole electrode layers are summarized in Table 2. Higher electrical resistance of the IH-immersion method electrode can be explained with the lower penetration depth of PPy into the membrane pores already filled with electrolyte.

<table>
<thead>
<tr>
<th>Membrane preparation method</th>
<th>Electrical resistance (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPI-immersion</td>
<td>4.5</td>
</tr>
<tr>
<td>MPI-vapor</td>
<td>3.8</td>
</tr>
<tr>
<td>IH-immersion</td>
<td>12</td>
</tr>
</tbody>
</table>

The measured electrical conductivity of the electrochemically synthesized DBS⁻-doped PPy electrodes (20 ± 2 S·cm⁻¹) is in good agreement with L. Bay *et al* [38] (19.8 S·cm⁻¹, slightly different conditions) and depended neither on the underlying membrane nor on the method of chemical synthesis or the thickness of the electrochemically synthesized layer.

### 3.4. Electrochemical properties

The difference of ion mobilities of the two electrolytes are illustrated by the cyclic voltammograms, recorded after 10 cycles at chosen scan rate for IH-immersion actuators soaked with 1 M LiTFSI and 1 M EMIBF₄ solutions in PC, respectively (Fig. 3 A, B). Keeping in mind that due to the bulky nature of DBS⁻ anions, they cannot leave the electrode during the reduction half-cycle [27], and considering the peak positions and the depreciation of activity at higher scan rates, it is obvious that Li⁺-cations from LiTFSI are by far the more mobile species.
Asymmetric behavior, seen on Fig. 3 B, is probably a more complex phenomenon illustrating the difficulties in moving bigger EMI$^+$ cations, the visually observable creep (resulting from uneven swelling and accumulation of EMI$^+$ cations inside of the electrode by the end of bending cycle), and also the partial transition to anionic (BF$_4^-$) mobility as an alternative way for charge compensation when EMI$^+$ cations cannot leave the electrode upon oxidation fast enough. The transition from one mobility type to another is also supported by the observation that the direction of displacement (at same polarity) becomes reversed by the 20th cycle and recovers temporarily its initial direction after some rest period if no voltage is applied between the electrodes. Similar behavior has been noticed by Yamato et al [39].

Frequency dependence of the polarization charge (negative charge shown on Fig. 4) indicates that on higher frequencies the electrodes cannot be fully oxidized or reduced in the timeframe of the cycle, and the exchanged charge strongly depends on the mobility of ions. As the absolute values of positive and negative charges were virtually the same, the polarization charge (Table 3) is calculated as an average of the absolute values of positive and negative charges exchanged during a full actuation cycle. Similar values obtained for the low frequencies confirm the immobility of DBS$^-$ anions (and also the constant doping level), which determines the maximal polarization charge.

Table 3. Exchanged charges (mC·cm$^{-2}$) for two electrolytes (IH-immersion) at different frequencies (Hz).

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Average charge of reduction and oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 M LiTFSI in PC</td>
</tr>
<tr>
<td>0.005</td>
<td>297.5</td>
</tr>
<tr>
<td>0.01</td>
<td>194.9</td>
</tr>
<tr>
<td>0.1</td>
<td>43.5</td>
</tr>
<tr>
<td>1.0</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Electrochemical doping level, calculated from the synthesis charge (IH-immersion, 4 C·cm$^{-2}$) and the maximum polarization charge (negative charge 298.3 mC·cm$^{-2}$ at scan rate 60 mV·s$^{-1}$) was found to be 0.16 which is close to that of L. Bay et al [38] (≈ 0.15, scan rate 2 mV·s$^{-1}$, PPy electrode thickness 10 µm). Apparently, the chemically synthesized “electrode” layer does not alter the properties of the electrochemically synthesized layer as compared to PPy deposited on more conventional electrode materials. Due to the low thickness and high porosity of the chemically synthesized inner layer, it is reasonable to conclude that the electrochemical specific charge storage capacity of the actuator is determined mostly by the doping level of the electrochemically synthesized layer.
3.5. Actuation parameters

All the prepared actuators exhibited relatively large displacement values, as depicted on Fig. 5. The bending displacement and blocking force of the actuators depend on the strain in the electrode material as well as the actuator geometry. For comparison of actuators with different displacement, measurement distances (5 or 12 mm from the fixed end), and of different thicknesses, only strain values calculated using Eq. (1) are presented. The differences are caused by different membrane types, different electrochemically deposited layer thicknesses, and different swelling ratios. Numeric actuation parameters were measured as the response to sinusoidal potential scans (3V peak amplitude) (Fig. 6). Different current values can be explained with the different mobility of electrolyte ions, different PPy layer thicknesses (synthesis charge 4 C·cm⁻² for IH-immersion versus 8 C·cm⁻² for MPI-immersion), and better ionic conductivity of the micro porous membranes [40].

No evidence of delamination was noticed for any actuators during actuation experiments for up to 1000 cycles.

3.5.1. Strain and strain rate

Actuators immersed in 1 M EMIBF₄ in PC solutions showed noticeable creep. Therefore, for better comparison, reversible strain is calculated using not the absolute displacement, but relative to the middle position of the full bending cycle. Strain values were calculated using actuator thicknesses measured after swelling in target electrolyte (Table 4).

Actuators, immersed in 1 M LiTFSI in PC solutions showed bending, characteristic of cation-mobile actuators, i.e. bending toward the positive electrode, but actuators, immersed in 1 M EMIBF₄ in PC, behaving initially as cation-mobile ones, reversed the displacement direction during the first tens of cycles (Fig. 7) apparently due to the transition to anionic (BF₄⁻) activity.

Table 4. Thicknesses of actuators after swelling in target electrolyte (µm).

<table>
<thead>
<tr>
<th>Method</th>
<th>Electrolyte</th>
<th>1 M EMIBF₄ in PC</th>
<th>1 M LiTFSI in PC</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPI-immersion</td>
<td>301</td>
<td>294</td>
<td></td>
</tr>
<tr>
<td>MPI-vapor</td>
<td>145</td>
<td>155</td>
<td></td>
</tr>
<tr>
<td>IH-immersion</td>
<td>419</td>
<td>417</td>
<td></td>
</tr>
</tbody>
</table>

The best strain values (Fig. 8) were achieved for the IH-immersion actuators with 1 M LiTFSI in PC (up to 4.4%), and compare well with those achieved by L. Bay et al [38] (2.5% without and up to 5.5% with 1-pentanol additive on electrochemical synthesis).
Actuators swelled in 1M LiTFSI in PC electrolytes had better strain rate (calculated from Eq. (2)) peak values and these peak values corresponded to higher frequencies (MPI-immersion 0.17 %·s⁻¹ at 1.9 Hz, MPI-vapor 0.63 %·s⁻¹ at 1.25 Hz and IH-immersion 0.56 %·s⁻¹ at 0.5 Hz) than those swelled in 1M EMIBF₄ in PC electrolytes (MPI-immersion 0.11 %·s⁻¹ at 0.19 Hz, MPI-vapor 0.06 %·s⁻¹ at 2.8 Hz and IH-immersion 0.03 %·s⁻¹ at 1.25 Hz).

3.5.2. Force output

Blocking forces were measured at a distance of 5 mm from the fixed end of the actuator. Comparison of the current (Fig. 6) and the blocking force (Fig. 9) shows (keeping in mind also the different synthesis charges) that charge to force ratio is better for the MPI-immersion than for the IH-immersion actuators. The differences in blocking force can be explained either by the different mechanical properties of the membranes or by the different membrane to electrode thickness ratio.

Frequency dependence of the blocking force for MPI-membranes (in Fig. 10) exhibits relaxation at low frequencies. The blocking force does not fall with increasing frequency as fast as the strain does, which can be caused by the more constrained ion movement as the bending of actuator is blocked. Absolute values of blocking force cannot be directly compared because of different actuator thicknesses.

4. Conclusion

Free-standing, air operated three-layer PPy-based actuators were prepared using novel metal-free chemical-electrochemical synthesis routes. The most important electrochemical and actuation parameters from the point of view of the evaluation of the synthesis method were characterized. It was shown that the chemically synthesized base layer enables the following well-controlled electrochemical synthesis of PPy without altering its properties as compared to deposition on metal electrodes. The benefits of the approach include the abatement risk of delamination, simplification of the actuator preparation procedure, while retaining the well tunable parameters characteristic of purely electrochemically deposited electrodes. The feasibility of the synthesis was investigated using a variety of optional methods; those yielding the highest reproducibility of good results were presented. No method/electrolyte combination was clearly better than others; the choice should depend on the target characteristics (strain, strain-rate, blocking force, etc).

The process could in principle be further optimized for particular application areas of the actuators, by tuning the membrane and electrode geometry [24], increasing force output using different dopants (like Na-4(6D)BS instead of NaDBS [27]), increasing strain by suppressing DBS-doped PPy anisotropy with additives like 1-pentanol [38], optimizing the electrolyte composition and PVdF membrane properties using different additives [40] or using some other membrane material altogether. To our best knowledge, this is the first description of the preparation of conducting-polymer based actuators using metal-free combined chemical-electrochemical synthesis routes. Several of the proposed chemical synthesis techniques suitable for two-sided porous non-conducting membranes are also novel, including low temperature electrochemical synthesis in mixed aqueous solutions (of water and MEG), membrane “painting” with the oxidizer agent, vapor-polymerization, etc.
Acknowledgements

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Vitae

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Figure captions

**Fig. 1.** Chronopotentiogram of the electrochemical synthesis. A – on in-house solid gel membrane (curve shape is typical for all methods), B – on stainless steel (AISI 316L) electrode (for comparison).

**Fig. 2.** SEM micrographs of the membrane. Surface after chemical synthesis (top row): A – MPI-immersion, B – MPI-vapor, C – IH-immersion; after electrochemical deposition (bottom row): D – IH-immersion, surface; E – IH-immersion, cross-section before swelling in target electrolyte; F – IH-immersion, interface between electrode and membrane.

**Fig. 3.** Cyclic voltammetry results for IH-immersion actuators: A – 1 M LiTFSI in PC, B – 1 M EMIBF$_4$ in PC; scan rate: (a) 60 mV·s$^{-1}$ (0.005 Hz), (b) 120 mV·s$^{-1}$ (0.01 Hz). For better comparison, the pseudo capacitance is calculated as current density divided by scan rate.

**Fig. 4.** Frequency dependence of the polarization charge for IH-immersion actuators. Actuator cycled with linear sweep between -3 ... +3 V. For clarity, only the (absolute) negative charge is shown here. A – 1 M LiTFSI in PC, B – 1 M EMIBF$_4$ in PC as electrolytes.

**Fig. 5.** Peak displacements of IH-immersion actuator (1 M LiTFSI in PC electrolyte, frequency 0.01 Hz, peak voltage 3 V). A – negative potential applied to the right side, B – positive potential applied to the right side.

**Fig. 6.** Current *versus* potential at frequency 0.1 Hz. A – IH-immersion, 1 M LiTFSI in PC, B – MPI-immersion, 1 M EMIBF$_4$ in PC.

**Fig. 7.** Strain as a function of voltage after about 50 working cycles. A – IH-immersion, 1 M LiTFSI in PC; the actuator deflects towards positively charged electrode. B – MPI-immersion, 1 M EMIBF$_4$ in PC; the actuator deflects towards negatively charged electrode. Voltage is measured on right clamp on Fig. 5. Positive strain corresponds to deflection toward left electrode on Fig. 5.

**Fig. 8.** Strain *versus* frequency for different electrolytes and synthesis methods. A – 1 M EMIBF$_4$ in PC, B – 1 M LiTFSI in PC; method: (a) MPI-immersion, (b) MPI-vapor, (c) IH-immersion.

**Fig. 9.** Blocking force *versus* voltage after about 50 working cycles. A – IH-immersion, 1 M LiTFSI in PC, B – MPI-immersion, 1 M EMIBF$_4$ in PC. Voltage is measured on right clamp on Fig. 5. Force direction corresponds to deflection direction on Fig. 7.

**Fig. 10.** Blocking force *versus* frequency for different electrolytes and synthesis methods; A – 1 M EMIBF$_4$ in PC, B – 1 M LiTFSI in PC; method: (a) MPI-immersion, (b) MPI-vapor, (c) IH-immersion.
References


Figure 4

Polarization charge (mC cm$^{-2}$) vs. Frequency (Hz)

- Curve A
- Curve B
Figure 9

The graph illustrates the relationship between voltage (V) and force (mN) over time (s). Two main curves are depicted:

- **Voltage**: A solid line representing the voltage changes over time.
- **A (Force)**: A dashed line indicating the force changes over time. It is labeled as 'A (Force)'.
- **B (Force)**: A dotted line showing another force change over time. It is labeled as 'B (Force)'.

The x-axis represents time in seconds (s), ranging from 0 to 20. The y-axes represent voltage (V) and force (mN), with their respective scales ranging from -3 to 3.
Figure 10