Producing and investigation of PEDOT films as electrodes of ionic electroactive actuators

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Abstract. Experimental samples of ionic electroactive actuators with poly(3,4-ethylenedioxythiophene) electrodes (PEDOT) have been developed and produced. Measurements of amplitudes of a displacement, frequency and power characteristics of produced actuators were carried out. The influence of the membrane solvent, as well as the influence of the EDOT polymerization time on the sample structure and the output characteristics of actuators, was determined.

1. Introduction
During recent years, the investigation of innovative materials for the development of actuators is of great interest, which leads to the emergence of some actuator technologies that may be suitable for automatic actuation. These alternative devices range from pneumatic muscle actuators, piezoelectric actuators to electroactive polymers. Promising materials are electroactive polymers (EAP). They are polymers that change shape and/or size when an electric field is applied. Such actuators are characterized by ease of manufacture, high mechanical flexibility and biocompatibility.

One of EAP types is ionic polymer-metal composites (IPMC). Structures based on IPMC represent synthetic composite nanomaterials, which consist of a porous ion-exchange polymer saturated with an electrolytic solution and with metal electrodes on both sides. Despite many advantages of such materials, expensive noble metals are needed to create electrodes in IPMC structures [1, 2].

One of ways to solve this problem is to use more affordable flexible electrodes. The result of the evolutionary development of IPMC structures are structures based on ionic polymer-polymer composites (IP2C), in which metal electrodes are replaced by organic [3, 4]. Such a system has great potential, since it combines the ability to develop flexible substrates with low costs, while maintaining the ability for electromechanical transductions, high compliance, lightness and softness of IP2C. One of representatives of such polymers is poly(3,4-ethylenedioxythiophene)/polystyrenesulfonate (PEDOT:PSS) [5].

2. Fabrication of IP2C actuators with PEDOT electrodes
The PEDOT:PSS conductive composition exhibits high p-type conductivity and manufacturability. Previously [3], the method of drop casting PEDOT:PSS water dispersion on the surface of a Nafion 117 membrane, soaked in a solvent, was used to create IP2C-actuators. Unfortunately, organic electrodes of IP2C -actuators fabricated with the help of this technology are destroyed during the rehydration of samples. Therefore, 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid was
used as a membrane solvent instead of water. The efficiency of electromechanical transductions decreases, since its viscosity significantly exceeds the viscosity of water.

For these reasons, in situ polymerization of 3,4-ethylenedioxythiophene (EDOT) was used in this work in order to obtain IP2C-actuators with PEDOT-electrodes, which consisted of the following stages:

- surface treatment of membrane strips of 3×0.5 cm in size with emery paper in order to improve adhesion of deposited thin films;
- washing the membrane strips with distilled water and their subsequent boiling in distilled water for 1 h;
- soaking of membrane strips in solutions containing 0.096 ml EDOT, 0.037 g PSS and 48 ml H2O for 1 h;
- removal of membrane strips from aqueous solutions followed by the addition of 0.99 g of FeCl3 to the flasks in order to carry out EDOT polymerization;
- dipping of membrane strips in flasks so that there is no contact with the inner walls;
- mixing the contents in flasks on a magnetic stirrer for different durations (15 min, 45 min, 1 h) – in situ polymerization itself;
- removal of samples from polymerization solutions and thorough washing in distilled water;
- boiling samples in 1 M H2SO4 for 1 h and in distilled water for 1 h.

It was found that PEDOT has a good adhesion to sulfonate-containing fluorocarbon matrices and gives the Nafion 117 surface a blue-black color. This may be due to the fact that during the polymerization process, the sulfonic acid groups of Nafion 117 can serve as counterions. Therefore, it is impossible to exclude polymerization inside the membrane. Good adhesion between Nafion 117 and PEDOT electrodes is confirmed by the possibility of rehydration of samples after their usage without degradation of any of them. The SEM images of the sample obtained by the in situ EDOT polymerization method for 45 min are shown in figure 1.

![SEM images of the cross-section (a) and the surface (b) of the sample.](image)

This morphological characteristic allows one to estimate the thickness of the thin electrode layer of the PEDOT film on the membrane surface. It is about 2 microns. The surface of the electrode turned out to be quite uniform, and there are no cracks on it that could lead to electrolyte leakage. For comparison, the thickness of the PEDOT:PSS layer deposited on the membrane surface by an irrigation of a water dispersion is about 10 microns.

3. Investigation of IP2C actuators

The block diagram of a bench for the investigation of IP2C samples is presented in figure 2. The investigated IP2C-actuator was fixed with probes, through which the voltage from the Agilent 33500B...
Series signal generator was applied. Bending of the IP²C-actuator was recorded with a L-GAGE laser displacement meter. Information from it was sent to an Agilent DSO-X 3014A oscilloscope and then to a PC.

![Image of block diagram](image)

**Figure 2.** Block diagram of the bench investigation of IP²C-actuators.

The principle of operation of IP²C-actuators is based on membrane transport processes. When an external voltage is applied to both sides of the IP²C-actuator, an electric field gradient is created in the membrane causing cations to move. This leads to differences in the concentration of ions in the membrane. An excessive mechanical pressure occurs near one of electrodes due to a diffusion of ions, which causes a bending of the IP²C actuator [3].

The dependences of bending of an IP²C-actuator with electrodes obtained by various methods on the applied voltage were investigated (figure 3). The IP²C-actuators with PEDOT:PSS electrodes, obtained by the irrigation method, were soaked with an ionic liquid. IP²C-actuators from PEDOT, obtained by *in situ* polymerization, were soaked with water. For comparison, IPMC actuators with platinum electrodes, also soaked with water, were investigated [4, 5].

IP²C-actuators, obtained by *in situ* EDOT polymerization, are capable to bend with amplitudes that are an order of magnitude larger than in the case of the irrigation method and even exceeding displacement amplitudes of IPMC actuators. With an increase in the polymerization time, the displacement amplitude of IP²C-actuators increases. This is due to the fact that the effect, which is caused by a decrease in the electrode resistance, is larger than the effect caused by an increase in the stiffness of samples.

As the frequency of the control signal increases, the displacement amplitude of the IP²C-actuator starts to decrease, then it begins to increase until it reaches a maximum at the resonant frequency and then decreases again (figure 4). Reducing the time of polymerization leads to a shift of the mechanical resonance to the region of higher frequencies. This is due to the fact that during measurements there is a loss of water from the membrane. Such a loss occurs easier through a less dense polymer electrode. All this leads to the fact that the IP²C-actuator has a higher resonant frequency due to loss of a greater amount of solvent.

![Image of figure 3](image)

**Figure 3.** Dependence of the displacement amplitude of actuators on the amplitude of a sinusoidal voltage at a frequency of 1 Hz.

In order to measure the force created by the IP²C-actuator, a constant voltage was applied to it, and its end moves from the original position and pressed on the analytical balance. An increase in the polymerization time leads to an increase in the force values, which is explained by an increase in the sample stiffness (figure 5). The value of the maximum force for IP²C-actuators obtained by the method of *in situ* EDOT polymerization is 4.6 mN. This is more than 2 times lower than that for IPMC-actuators. Breakdown of the IP²C-actuator, obtained by the irrigation method, occurs at a constant voltage exceeding 3 V.

IP²C-actuators, obtained by the method of *in situ* EDOT polymerization for 1 h, are characterized by the highest efficiency of electromechanical transductions. Thus, their continuous operation in the
air was investigated. Such IP\textsuperscript{2}C-actuators can deform within 4 min when a constant voltage of 1 V is applied, and the greatest displacement (8 mm) occurs within the initial 10 s (figure 6). For comparison, IP\textsuperscript{2}C-actuators, obtained by the irrigation method, reach the maximum value of displacement after 10 s of operation. And the value is an order of magnitude smaller than in the case of the polymerization method. The displacement is almost unchanged for further supply of voltage.

Figure 4. Dependence of the displacement amplitude of IP\textsuperscript{2}C-actuators on the frequency at an amplitude of sinusoidal voltage of 5 V.

Figure 5. Dependence of the force of IP\textsuperscript{2}C-actuators on constant voltage.

Figure 6. Dependence of the displacement of IP\textsuperscript{2}C-actuators on time at a constant voltage of 1 V.

Figure 7. Dependence of the displacement amplitude of the IP\textsuperscript{2}C-actuator, obtained by \textit{in situ} EDOT polymerization for 1 h, on time with an amplitude of sinusoidal voltage of 5 V and a frequency of 1 Hz.

It can be seen from figure 7 that when a sinusoidal voltage is applied during the first 20 min of operation, the IP\textsuperscript{2}C-actuator bends with an average amplitude of 5 mm, and the maximum displacement amplitude is reached after 10 min. Over the next 20 min of operation, the displacement amplitude decreases by about 2 times. A gradual decrease in the amplitude of displacement is observed during last 20 min. Output characteristics of IP\textsuperscript{2}C-actuators are summarized in table 1.

4. Conclusions
The technology of producing of polymer PEDOT electrodes by \textit{in situ} polymerization on the surface of an ion-exchange membrane is presented. It is shown that the greatest displacement amplitudes are achieved due to the usage of water as a solvent in IP\textsuperscript{2}C-actuators.
Table 1. Output characteristics of IP²C-actuators.

| Type of actuator      | Maximum displacement amplitude (at 1 Hz), mm | Resonance frequency, Hz | Maximum force, mN |
|-----------------------|---------------------------------------------|-------------------------|-------------------|
| IP²C (PEDOT:PSS)      | 1.7                                         | 17                      | 2                 |
| IP²C (PEDOT/15 min)   | 7.2                                         | 16                      | 2.2               |
| IP²C (PEDOT/45 min)   | 10.5                                        | 12                      | 3                 |
| IP²C (PEDOT/1 h)      | 11.8                                        | 10                      | 4.6               |

It is shown that the value of the displacement amplitude, the position of the mechanical resonance and the magnitude of the generated force are influenced by the EDOT polymerization time. This is due to the fact that an increase in the polymerization time leads to a decrease in the resistance of electrodes and an increase in the film density and the sample stiffness.

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