Creating of thin film sensor layer by electropolymerization

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Abstract:
This paper deals with the process of electropolymerization. The electropolymerization is the method used mainly for creating thin film sensor layers. In this paper the creating of sensor layers by electropolymerization on interdigital structure is discussed. Three methods of electropolymerization are demonstrated. The results of experiments with creating sensor layers are in the next part. The problems with electropolymerization are described in the last part of this paper.

INTRODUCTION

Electropolymerization is a process for creating polymer thin film layers on interdigital structures. The basic arrangement and schema for electropolymerization is demonstrated in figure 1. This system includes power supply, measuring equipments, platinum electrode (Pt), interdigital structure (IDC) and tube with the solution of vinylcarbazole. Platinum electrode and interdigital structure that forms the second electrode are plunged in the solution of $LiClO_4$ + vinylcarbazole + CH_3CN. This solution is necessary to be shaken and bubbled by nitrogen before application process. Pt electrode is connected to the negative pole and interdigital structure is connected to the positive pole of DC power supply. After power supply is connected, the thin film of vinylcarbazole monomer starts to grow on the interdigital structure. The monomer of vinylcarbazole comes to polymer by incidence of voltage or current. The green thin film of polymer is created on the interdigital structure. This interdigital structure with polymer thin film can be used for humidity or gases sensors.

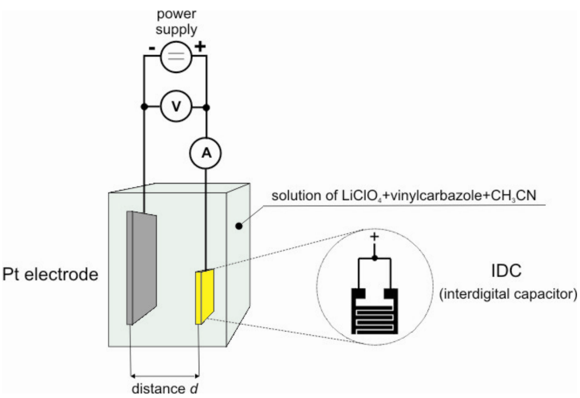

Fig. 1: The basic arrangement for electropolymerization.

The practical measurement station consists of DC source, signal generator, measure equipments and scope is shown in figure 2. The Pt electrode and IDC are held in special jig and are plunged into the solution with vinylcarbazole monomer.

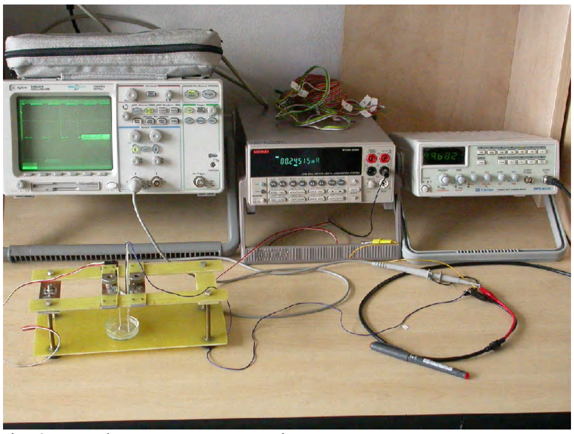

Fig. 2: The measurement station.

The clear interdigital structure before process of electropolymerization is shown in figure 3. This figure shows the gap and gold electrode of the interdigital structure with 2400 zoom.

Fig. 3: The clear zoomed interdigital structure.

The green layer of polymer is created during the electropolymerization. Three basic methods are possible to use for creating of polymer layer by electropolymerization. The first method is keeping the constant potential between Pt electrode and interdigital structure. The second method is keeping the constant current during all process of electropolymerization. The pulse signal generator instead of DC source with different magnitude of voltage, frequency and offset is used for the third method.

CONSTANT POTENTIAL METHOD

Method of constant potential consists in the keeping the constant voltage between Pt electrode and IDC. Whole process of electropolymerization is functional in voltage range between 1,5 V and 3 V. The polymer layers are not created outside this voltage range. The best efficiency is achieved for the voltage of 2,5 V. The thickness of polymer layer is possible to control by the voltage magnitude, time of the plunge and distances of electrodes.
Distance of electrodes does not have the influence on the process of electropolymerization. Identical polymer layer is created if no other conditions are changed.
The thickness of polymer layer is directly proportional to the time of plunge but the polymer layer can be striped from surface because of the too thick polymer layer.

The voltage of 1,5 V and the time of plunge of 60 s cause creation of the very thin film polymer layer on the gold electrode and in the gap. This example is shown in figure 4.

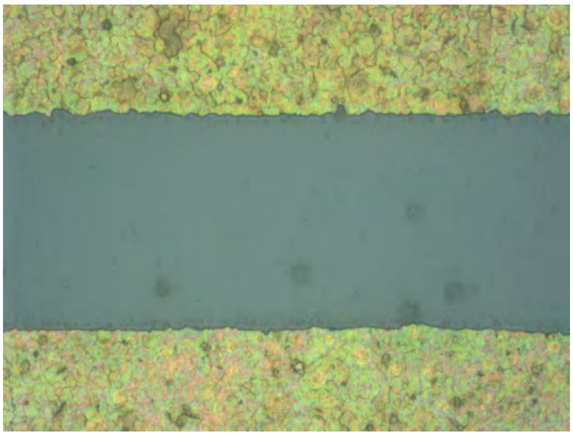

Fig. 4: The created polymer layer for the voltage of 1,5 V and the time of plunge of 60 s.

The thick polymer layer on the surface of IDC is created for the voltage of 2,5 V and the time of plunge of 60 s. This thick polymer layer is thicker on the gold electrodes than in the gap (Fig. 5). The thickness of polymer layer is 3 μm in the gap. The created polymer layer is porous without cracks; on the surface there are white crystals sporadically.

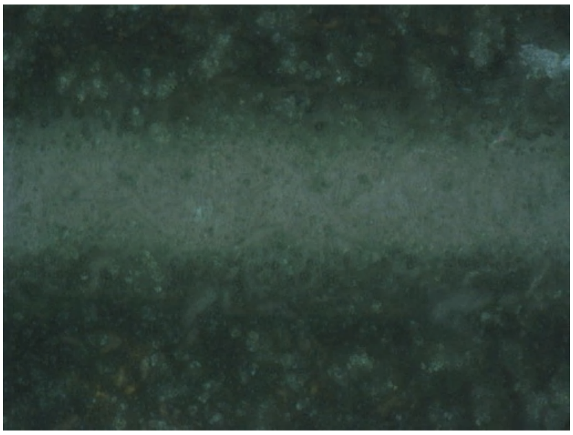

Fig. 5: The created polymer layer for the voltage of 2,5 V and the time of plunge of 60 s.

The polymer layer on the gold electrode is the thickest for the voltage range from 3,25 V to 3,75 V. This layer contains many cracks. The polymer layer in the gap grows from the middle to the edge and is thin and porous.

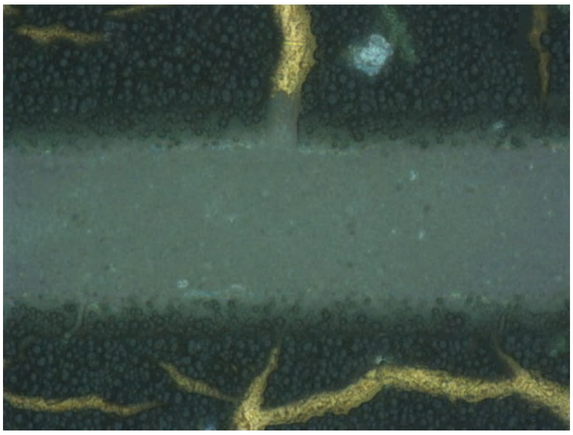

Fig. 6: The created polymer layer for the voltage of 3,5 V and the time of plunge of 60 s.

CONSTANT CURRENT METHOD

The constant current between Pt electrode and interdigital structure was kept for the method of constant current. The process of electropolymerization is functional for the current range from 2 mA to 4 mA. The best results are for the current of 4 mA. Higher currents cause several problems like washing off the polymer layer from IDC and Pt electrode becomes black. The thickness of polymer layer can be controlled by magnitude of current and the time of plunge of electrodes in the solution. The thicker polymer layer is created because of longer time of plunge. For the time of plunge more than 240 s, the polymer layer is washed off.
Distance of electrodes does not have any influence on the process of electropolymerization. Identical polymer layer is created if no other conditions are changed.

The beginning of electropolymerization process starts from the current of 2 mA. For this current the gold electrode is covered by the thick polymer layer. In the gap the layer is thinner and porous (Fig. 7).

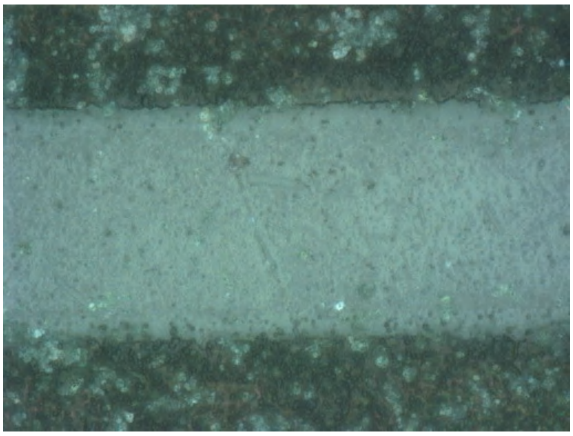

Fig. 7: The created polymer layer for the current of 2 mA and the time of plunge of 60 s.

For the current of 4 mA the thickest polymer layer is created on the gold electrode and in the gap (Fig. 8). The gap is not completely covered. The polymer layer is very porous and covered by white crystals.

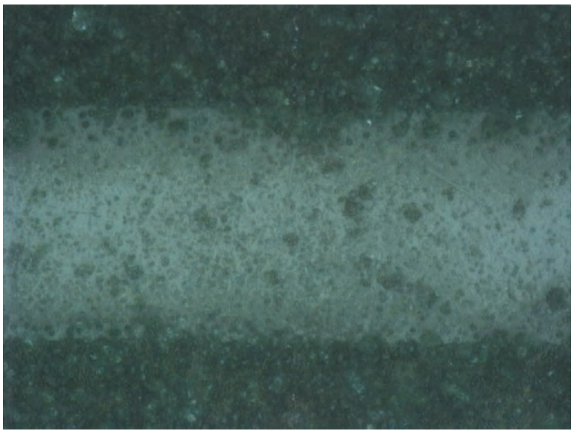

Fig. 8: The created polymer layer for the current of 4 mA and the time of plunge of 60 s.

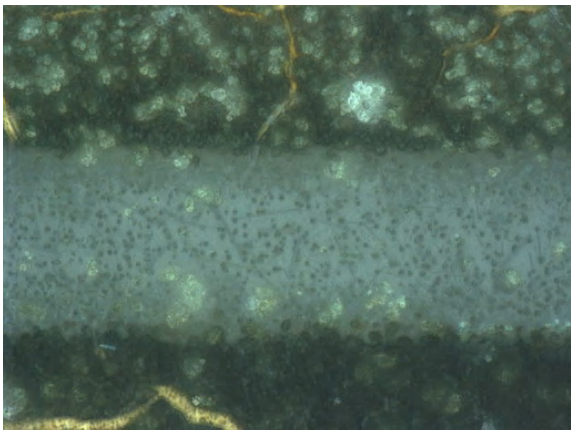

Fig. 9: The created polymer layer for the current of 2 mA and the time of plunge of 180 s.

The interdigital structure that was plunged in the solution for 180 s with the current of 2 mA is in figure 9. The polymer layer is on the gold electrode and grows in gap but the polymer layer is not in the middle of the gap. The polymer layer has crystal structure with many cracks.

PULSE SIGNAL METHOD

The basic arrangement and schema for method of pulse signal is the same like in figure 1 but power supply is replaced by a generator of square wave with possibility to set up the frequency, pulse ratio and offset of output signal. The thickness of a polymer on the interdigital structure can be controlled by the magnitude of the voltage, offset, pulse ratio, time of a plunge into the solution, distances of electrodes and frequency of input signals.
The square wave signal with different pulse ratio, frequency and offset was used for this method. The process of electropolymerization was functional for offset signal from 1,6 V to 2 V and for magnitude of the output voltage (peak – peak) from 2 V to 3 V. The next important parameters are the frequency and pulse ratio. For example, the low frequencies (about Hz) are necessary to use for pulse ratio 1:1 and the high frequencies (about kHz) are possible to use for the pulse ratio 8:1. With higher pulse ratio there is possible to use higher frequencies. The thickness of the polymer layer is not controlled by frequencies but by the offset and by the time of plunge. But the appearance of the polymer layer is possible to control by frequencies because for some frequencies the structure is porous and contain the cracks. For the longer time of plunge the polymer layer is thicker, smooth and without crack.

Example of the curve of output signal from generator for pulse ratio 1:1 is shown in figure 10.

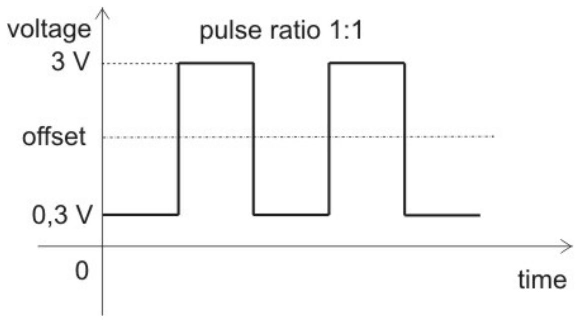

Fig. 10: The output square wave signal from generator with pulse ratio 1:1 and offset 1,6 V.

For the pulse ratio 1:1 the polymer layer is created for frequencies from 1 Hz to 5 Hz. For higher frequencies the process of electropolymerization is not possible. The thin green polymer layer covers the gold electrode; no polymer layer is in the middle of the gap (Fig. 11). The surface of polymer layer is covered by white crystals.

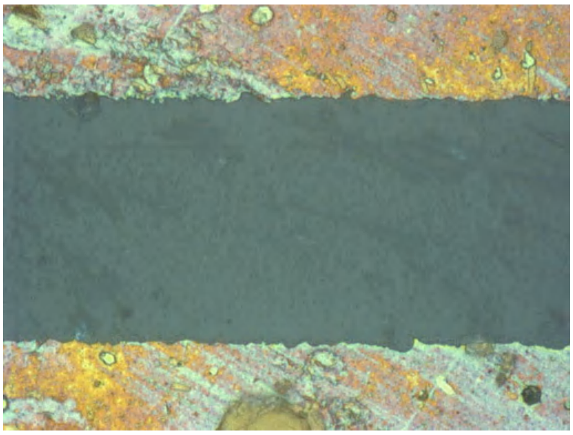

Fig. 11: The created polymer layer for the frequency of 5 Hz, the time of plunge of 60 s and the pulse ratio 1:1.

For the pulse ratio 2:1 and frequencies from 1 Hz to 5 Hz the thick polymer layer is created on the surface of interdigital structure (Fig. 12). This layer is on the gold electrode and in the gap but is porous and with small cracks. For higher frequencies the polymer layer is very thin and porous. There is practically no polymer layer in the middle of the gap.

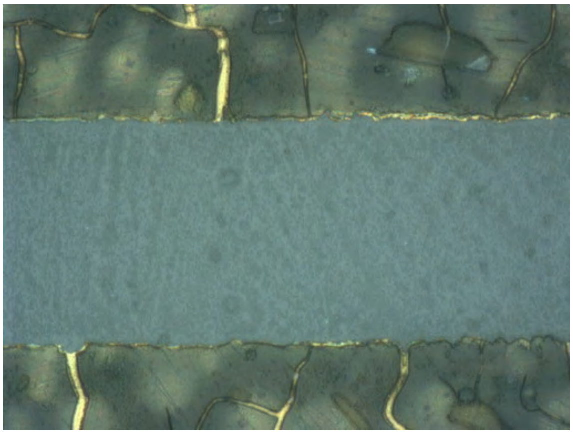

Fig. 12: The created polymer layer for the frequency of 5 Hz, the time of plunge of 60 s and the pulse ratio 2:1.

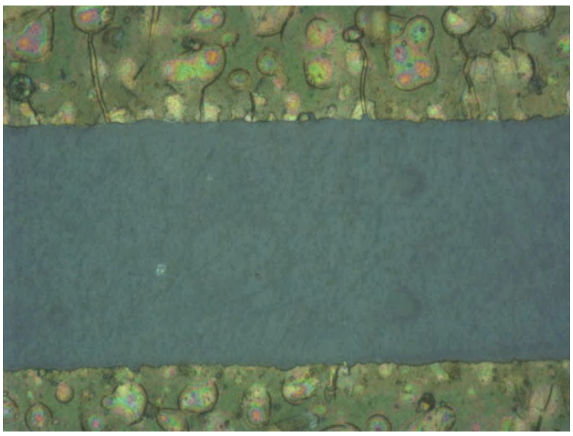

Fig. 13: The created polymer layer for the frequency of 5 Hz, the time of plunge of 60 s and the pulse ratio 3:1.

For the pulse ratio 3:1 and frequencies from 1 Hz to 10 Hz the created polymer layer is thin, porous but without cracks (Fig. 13). The thin layer is created on the gold electrode and in the gap. For frequencies about kHz the interdigital structure is not covered by any polymer layer.

For the pulse ratio of 8:1 and frequencies from 1 Hz to 10 Hz the gold electrode and the gap are covered by the thick polymer layer (Fig. 14). The layer on the gold electrode is smooth with small cracks. The layer in gap is porous and without cracks. For frequencies about kHz the thick porous polymer layer is created. This layer contains cracks and white crystals on the gold electrode and in the gap.

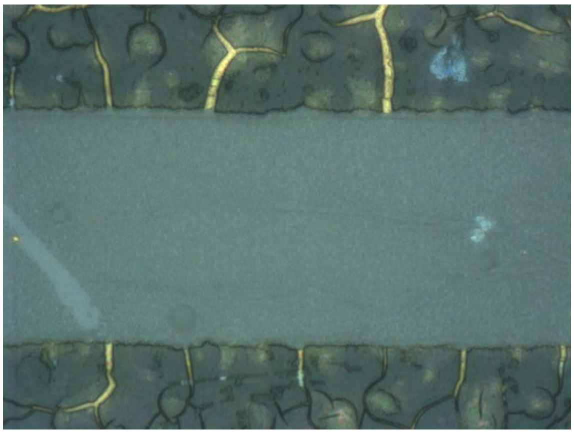

Fig. 14: The created polymer layer for the frequency of 5 Hz, the time of plunge of 60 s and the pulse ratio 8:1.

CONCLUSIONS

Several experiments with electropolymerization were carried out depending on voltages, currents, frequencies, distances of electrodes and time of plunge. The methods of constant potential and pulse signal are possible to use for creating of polymer sensor layers. The method of constant current didn't show sufficient results because the created polymer layers are more porous, the surface is rough and uneven. The range of currents is very narrow (2-4 mA) where the electropolymerization process is controlled.

The method of constant potential is controlled in the voltage range of 1,5 – 3 V and for this range the best results are achieved. The layer of polymer is created on the gold electrode and in the gap of the interdigital structure. The thickness of polymer layer is controlled by the voltage magnitude and the time of plunge. For the method of pulse signal satisfactory results are also achieved. The thickness and the appearance of surface of polymer layer are controlled by voltage magnitude, offset, frequency and pulse ratio. The polymer layer is created in the gap of interdigital structure. Disadvantage of this method is that many

parameters have influence on whole process of electropolymerization.
The verification of the created polymer layer in the gap of interdigital structure is shown in figure 15. There is the scratch in the polymer layer that was found after electropolymerization. The thickness of green polymer layer is on the gold electrode thicker and in the gap thinner. The thickness of created polymer layer is from the 100 nm to 10 μm.

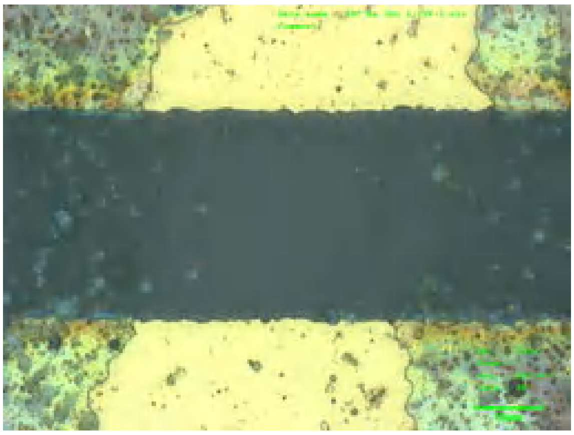

Fig. 15: The green polymer layer on the gold electrode and in the gap of interdigital structure.

Sometimes white crystals grow on the surface of polymer layer during electropolymerization (Fig. 16). These white crystals are created on the surface if the solution of vinylcarbazole is not bubbling by nitrogen and after electropolymerization the sample of interdigital structure is not washed in isopropylalcohol. The samples of interdigital structure should be dried at the shortest time after washing.

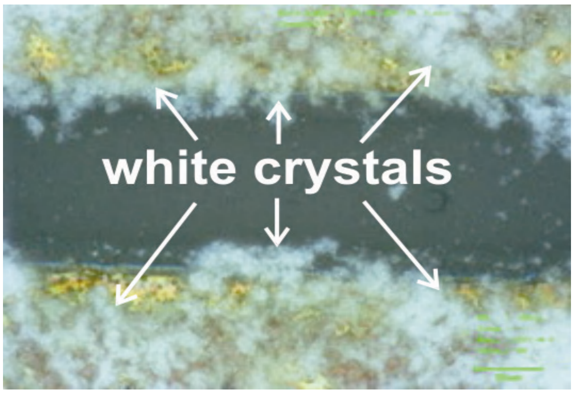

Fig. 16: The white crystals on created polymer layer.

The cracks of created polymer layer were detected on the edge of the gold electrode in a detail inspection (Fig. 17). The cracks have different size and occur irregularly. These cracks can be caused by a quick drying.
The polymer layer in the gap is sometimes porous or smooth. The porous layer depends on the voltage, current, frequency, time of plunge and the cleanness of interdigital structure.

Generally, it is possible to claim that the polymer layer is created on the whole interdigital structure if certain requirements are achieved by the process of electropolymerization.

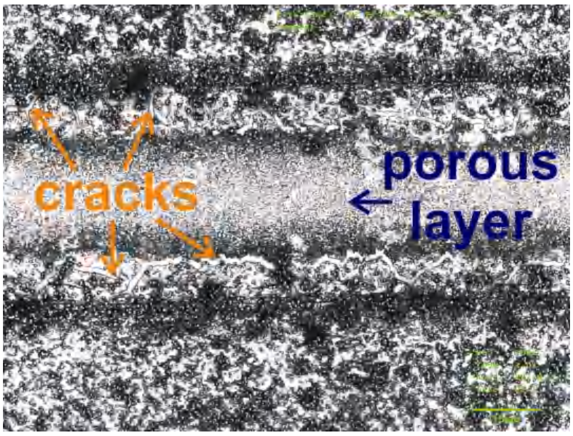

Fig. 17: The created porous polymer layer with cracks.

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