

COPPER ELECTRODEPOSITION ON INSULATORS (PLASTICS) USING HIGHLY CONDUCTIVE POLYPYRROLE FILMS

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Abstract: - In the present work we have studied the use of polypyrrole (PPy) as a precoat for the metallization of insulators. In particular, we etched ABS and FR4 with immersion in a solution containing $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and then made their surface conductive simply by adding to that solution an aqueous solution containing pyrrole, thus resulting in the chemical polymerization of pyrrole into polypyrrole and creating a new ABS/PPy and FR4/PPy electrode. The process was completed without using any toxic chemical agents used for etching in the conventional industry. From our experiments we have concluded that the polypyrrole-modified surfaces were conductive enough to allow the copper plating of the specimens at a later stage. Several parameters of the process at a laboratory level were studied.

Key-Words: - Conductive polymers, polypyrrole, insulators, copper electrodeposition.

1 Introduction

In recent years, intrinsically conductive polymers (ICP) have attracted much attention not only from a theoretical point of view but also in applied science and technology. Among others, polypyrrole (PPy) is one of the most widely used conductive polymers, due to its high chemical and physical stability, low toxicity of the monomer (i.e. pyrrole – Py) and its easy chemical or electrochemical synthesis, even in aqueous solutions [1].

ICPs have a number of interesting features that make their application in industry particularly attractive. The uses proposed include light emitting diodes, electrodes in rechargeable batteries, electrochromic displays, metallizing of plastics, printed circuit technology, antistatic coatings, corrosion protection, membrane separation etc [2],[3],[4].

Polypyrrole can be prepared by chemical or electrochemical oxidation. By inserting doping anions like PTS (para-toluene-sulfonic acid) PPy's conductivity is controlled according to the mechanism that is presented in Fig. 1. Chemical polypyrrole doped with PTS, showed high specific conductivity of the order of 10^2 S/cm, [4], [5], [6].

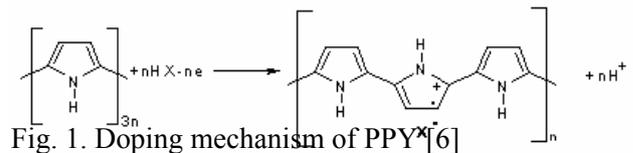


Fig. 1. Doping mechanism of PPy [6]

The structure of polypyrrole has been found to be one-dimensional as well as two-dimensional, depending on the conditions of synthesis [7],[8].

2 Problem Formulation

The conventional industrial methods for copper electrodeposition are usually based on an initial step of electroless metal deposition taking place on a catalyzed substrate surface (Pd). These methods demand many steps in order to achieve the desired quality, and also require hazardous solutions, like sulfuric-chromate acid, complexing agents (like EDTA), formaldehyde, and precious metal catalysts (i.e. Pd).

The production, use and disposal of these compounds received much regulatory attention due to their toxicity. The majority of these compounds are confirmed or suspected human carcinogens, and there is the tendency their use to be completely banded in the future.

3 Problem Solution

Our team has concentrated its efforts in developing a new simpler, cost-effective and environment-friendly method for copper electrodeposition. In the present work we have studied a conductive polymer of pyrrole as precoat on several insulators (ABS and FR4), in order to replace conventional industrial methods.

We studied the effect of several factors (etching time, pre-treatment of the substrate) to the copper plating process and reached to some conclusions concerning the optimization of the whole process.

3.1 Experimental - Materials

Our method is based on producing chemically in situ precoat of a conductive PPy film on the non-conductive substrates ABS (Acrylo-Butadiene-Styrene) and FR4 (glass reinforced epoxy resin).

This alters the surface from insulating state to a conductive one and afterwards, copper is electrodeposited. So, a new electrode ABS/PPy/Cu, FR4/PPy/Cu is formed.

Materials - PPy synthesis

Polypyrrole was synthesized from aqueous solutions of pyrrole monomer with chemical oxidation by using ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as oxidant and doped with PTS (para-toluene-sulfonic acid) [1], [14].

Preparation of specimens

For our experiments standard specimens of ABS and FR4 with dimensions 2,5 x 2,5 cm have been coated. All the specimens have been etched by immersion in the oxidant solution for 30 min.

For copper deposition two baths were used:

Bath A: 150 g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 50 g/L H_2SO_4 , 50 g/L $\text{CH}_3\text{CH}_2\text{OH}$ (EtOH).

Bath B: 240 g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ $\dot{\eta}$ 61,104 g/L total copper, 70 g/L H_2SO_4 , 0,12 g/L HCl, 5 g/L brightener

Deposition of PPy coatings

First, ABS and FR4 specimens are etched by immersion for 30 min in firmly agitated aqueous solution containing 8% pv $(\text{NH}_4)_2\text{S}_2\text{O}_8$. Ammonium persulfate also acts as an oxidant in the polymerization stage that follows. PPy is polymerized on ABS/FR4 surface, from an

appropriate optimized solution that contains 3.6% pv pyrrole and 4.4% pv PTS that acts as a dopant. By that, a new electrode is formed that can be electroplated.

Copper electroplating

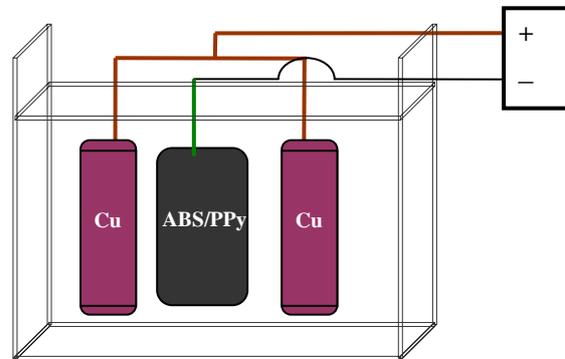


Figure 2 – Setup for copper plating of the ABS/PPy and FR4/PPy electrode

The ABS/PPy electrode is electroplated using the electrolytic cell shown in figure 2 that contains a copper ion bath. Copper is deposited onto ABS/PPy surface and an ABS/PPy/Cu sample is formed. The electrodeposition process was monitored potentiostatically.

The copper plating of FR4 substrates was conducted in the same cell with the same procedure.

3.2 Test methods

We have studied the effect of etching and other factors on the total copper-plating time and on the quality of the copper film.

We have measured the current during the copper electrodeposition of ABS and FR4 substrates.

The time needed for the metallization of these specimens was also recorded.

Finally, microscopic inspection of ABS specimens was performed, and their surface structure was studied by using X-rays Photoelectron Spectroscopy (XPS).

3.3 Results – Discussion

Etching time effect

The changes in the time needed for the copper plating of ABS/PPy electrodes in relation to the etching time, are shown in Table 1.

Etching time (min)	Time for metallization
15'	5:29'
30'	2:11'
45'	1:29'

Table 1 – Time needed for copper plating vs. Etching time
 ABS specimens metallised under 0.022 A/cm²
 (substrate surface: 1256 mm²)

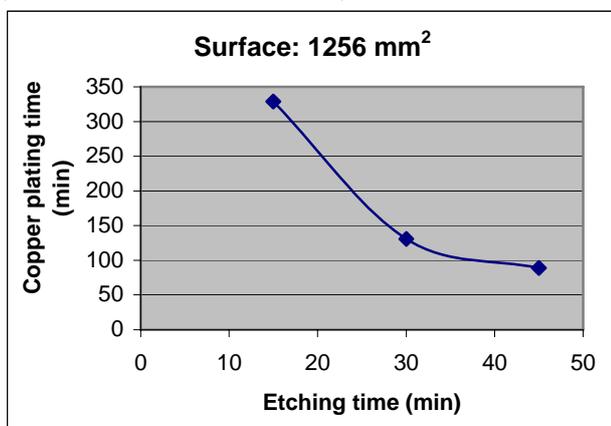


Fig. 3 – Time needed for copper plating vs. Etching time

As we can see from Table 1 an increase in etching time results in a relative decrease in the time needed for metallization, until a certain point. After that certain point, the etching time effect on the metallization total time becomes less important.

In particular, the doubling of the etching time from 15' to 30' results in the reduction of the total copper plating time in less than half.

When we tried to further increase the etching time by another 15' (to a total of 45'), the decrease in the total metallization time was less than what one would expect if the {Etching time – Metallization time} relation was linear.

This indicates that there is a limit in the results of etching of the substrate, after which there is no significant change of the substrate's surface morphology. The optimized time we found out was 30' of etching in aqueous solution containing 8% (NH₄)₂S₂O₈.

Macroscopic examination of the metallization process

The macroscopic examination of the plating process showed that the copper front propagates in a semi-circular manner from the point of electrical contact with the power source of the cell.

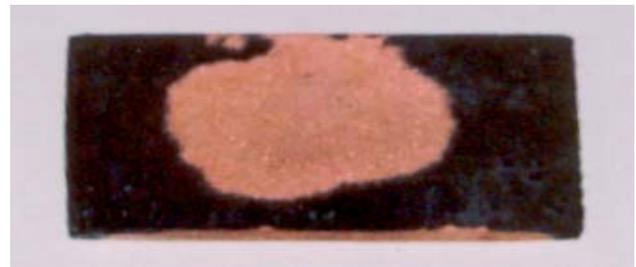


Fig. 4. Photograph of a specimen during the copper electroplating

This indicates that the copper front prefers to propagate through the high conductivity copper already placed on the substrate that through rest of the PPy-covered surface (which, even though it has enough conductivity to allow the metallization, has much lower conductivity than copper).

As a result we tried to increase the conductivity of the PPy-covered surface in order to decrease the total copper plating time.

Pre-treatment with AgNO₃

The effect of pre-treatment of the substrates with AgNO₃ was examined.

Experiments were conducted in which FR4 specimens, after being covered with PPy film, were immersed in AgNO₃ 0,1 N solution for 10 minutes before the metallization started.

The results of these experiments showed a very big decrease in the total time needed for the metallization, probably due to the increase of the PPy layer conductivity because of the diffusion of Ag atoms in it.

In particular, 10' immersion in the AgNO₃ 0,1N solution resulted in a 50% decrease of the metallization total time for a 2,5 x 2,5 cm FR4 specimen.

Rate of copper electrodepositing

The rate of copper electrodepositing is constant during the process and it was found to be about 0,0030 mg/min.

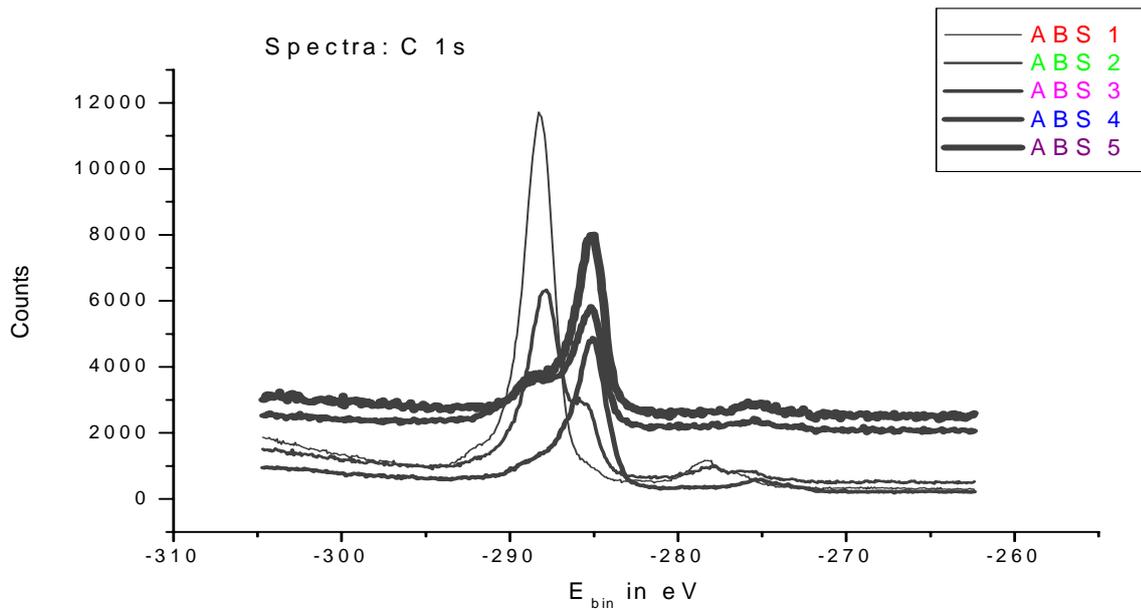


Fig. 5 XPS full scan spectrum of C 1s in each stage of the metallization (copper plating) process.

We also attempted to plate the ABS/PPy electrode in a nickel bath without success. The overpotential of nickel deposition on PPy is very high compared to the overpotential of copper on PPy [9].

XPS spectra

In figure 5 above, the XPS spectrum of C1s in each stage of the process is shown: ABS 1 (ref. specimen, without any treatment), ABS 2 (after the etching stage), ABS 3 (after the PPy coating), ABS 4 (after the copper electroplating) and ABS 5 (after the electroless copper deposition).

The presence of PPy (bond energy 284,7 eV) is confirmed at the C1s spectrum of ABS 3. Despite the existence of copper deposit on the specimens after the electroplating and the electroless deposition the ABS 4 and ABS 5 still show the existence of PPy (even though the PPy spectrum should be covered by the copper which resides on it). This happens probably due to the diffusion of copper atoms in the PPy film.

Comparison of conventional methods to our laboratory method

Our laboratory method offers an attractive alternative compared to the conventional methodology as shown in table 2.

Conventional Industrial Method	Our Method (laboratory scale)
Degreasing	Polymer etching with $(NH_4)_2S_2O_8$
Polymer etching (chrome-sulfuric acid)	In situ PPy chemical deposition
Rinsing	Rinsing (water)
Immersion in $PdCl_2$ - solution	Drying
Surface activation / reduction of Pd_2 by $SnCl_2$	Electrodeposition of Copper
Electroless Copper or Nickel plating with the use of formaldehyde and a complexing agent (EDTA)	Further processing
Degreasing ($10\%H_2SO_4$)	
Rinsing	
Electrodeposition of Copper	
Further processing	

Table 2: Flow sheet of our method and the conventional industrial for ABS metallizing

4 Conclusion

The results first of all prove that the ABS/PPy and the FR4/PPy electrode has sufficient conductivity to allow the copper plating

The front of the copper plating propagates in a semicircular manner starting from the point of the electric contact of the ABS/PPy [FR4/PPy] electrode with the current source.

The mechanism of copper deposition on PPy is different compared to the mechanism of copper ion deposition on a metal electrode.

The XPS spectra showed that during copper plating, copper atoms diffuse in the PPy coating.

An increase in etching time as well as a simple immersion in AgNO₃ solution seems to have a great impact on the total time needed for the metallization, without adding any complicated steps in the process.

Our method developed on a laboratory scale has advantages over the conventional methods of insulator's metal plating. It is exceptionally simple, energy - saving and environmentally friendly.

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The electrodeposition of copper on composite conductive polymer polypyrrole/polystyrenesulfonate PPy(PSS) has been studied. The morphology of copper deposits was investigated in the presence of thiourea and other additives. It has been found that in the presence of thiourea in the solution, the rate of copper deposition on a PPy(PSS) substrate is slightly inhibited but the rate of copper stripping is faster than in its absence. The Electrochemical Quartz Crystal Microbalance (EQCM) technique allowed us to simultaneously monitor voltamperometric and resonance frequency vs. potential or time cha