



Potentiostatic electrosynthesis of polypyrrole film onto silicon support

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Abstract

This work reports the electrochemical synthesis of polypyrrole (PPy) films onto silicon (Si) support in an organic solution using potentiostatic mode of electrodeposition. Electrodeposition of PPy was conducted under oxidative conditions; the current transient curve, taken at constant potential of 1.1 V, was discussed. The microstructure of the polypyrrole (PPy) films obtained is examined by SEM and AFM.

Keywords: oxidation, polymerization, potential, pyrrole.

1. Introduction

Conductive organic polymers, due to their structure, electrical conductivity and specific surface area of the polymer film, constitute a family of materials required in many application areas. They act as supports for the various metals to form composite films, thus acquiring high electrocatalytic properties which make these materials an alternative of choice for many applications where the use of catalysts in the metallic state is limited by their high cost, such as fuel cells and biofuel cells.

These polymers can be synthesized by oxidative polymerization either chemically or electrochemically. Of the organic monomers leading to electronically conductive polymers, pyrrole (Py) is the easiest to oxidize

[1-3]. It was first synthesized in 1916 by Angeli and his group. The synthesis was carried out by chemical oxidation of pyrrole in the presence of H_2O_2 and the resulting product, called "Black Pyrrole", was in the form of an amorphous powder. However, in order to better control the structure of the polymer, and thus its properties, electrochemical polymerization, commonly known as "electropolymerization", is the most appropriate synthesis method. It should also be noted that among the parameters influencing electropolymerization, the applied potential can play a determining role in the quality of the polymer formed in terms of density, continuity, adhesion and microstructure of the deposit [4- 5].

Herein, we report the synthesis of polypyrrole on silicon supports via electrochemical method under potentiostatic deposition mode. The evolution of current transient as a function of time at constant applied potential are discussed and the microstructure of the as-formed PPy films are examined by microscopy via SEM and AFM techniques.

2. Experimental

Electrochemical experiments were conducted in a conventional three-electrode cell at room temperature. Platinum (Pt) wire and saturated calomel electrode (SCE) $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}$ (3M) were used as the counter and reference electrode, respectively.

Polymerization of pyrrole was accomplished under galvanostatic control on n-doped silicon (Si) wafer from an organic solution of 5 mM pyrrole and 0.1 M lithium perchlorate (LiClO_4) dissolved in acetonitrile (CH_3CN). During preparation of the electrode, the projected surface area of the Si substrate was 0.4 cm^2 .

3. Results and discussion

3.1. Study of the polypyrrole stability on silicon support

In order to verify the stability of the PPy film obtained on a new material (silicon), we studied by cyclic voltammetry the electrochemical behavior of our monomer in an organic medium on a silicon electrode. As the electropolymerization of the monomer is carried out by anodic oxidation, the field of study chosen is located in the anodic zone. Figure 1 shows the voltammogram for a $10^{-1} \text{ M CH}_3\text{CN}/\text{LiClO}_4$ solution containing 5 mM of pyrrole, recorded at a scan rate of 50 mV/s.

During the first scan, a very intense peak is observed around 1 V/SCE, corresponding to the oxidation of the monomer (Py) into its cation radical which leads to the formation of the dimer adsorbed on the surface of the electrode. During the return scan, there is a characteristic crossing of the nucleation-growth phenomena of the polypyrrole.

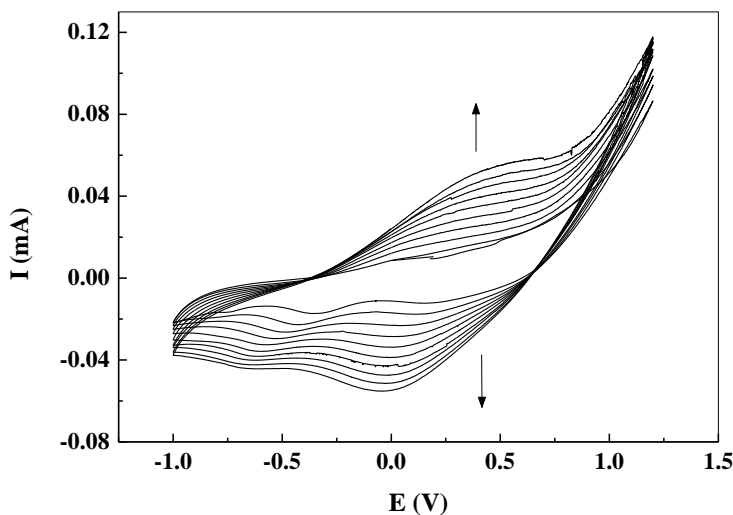


Figure 1. Cyclic voltammetry of pyrrole electropolymerization on silicon in 0.1M CH₃CN/ LiClO₄ containing 5 mM of pyrrole. Scan rate = 50 mV/s

We also note an increase in the current intensity of the oxidation and reduction peaks. This increase in oxidation and reduction currents is explained by the growth of the PPy film on the silicon electrode surface.

After having synthesized the polypyrrole film on silicon, we proceeded to study the PPy electroactivity by cyclic voltammetry, in a monomer-free solution (0.1 M KCl). Figure 2 presents the voltammogram obtained at a scanning speed equal to 20 mV/s.

The presence of large anodic and cathodic waves shows that the deposits are electroactive, stable and exhibit good redox behavior. The redox property of polypyrrole is related to the processes of insertion/expulsion of anions and cations. The ion present in the supporting electrolyte easily diffuses inside and outside the polymer during redox processes to neutralize the charge of the polypyrrole film.

We also note that the positions of oxidation and reduction peaks are different. The potential difference $\Delta E = |E_{pc} - E_{pa}|$ is not zero, which shows that the polymeric film PPy has good reversibility.

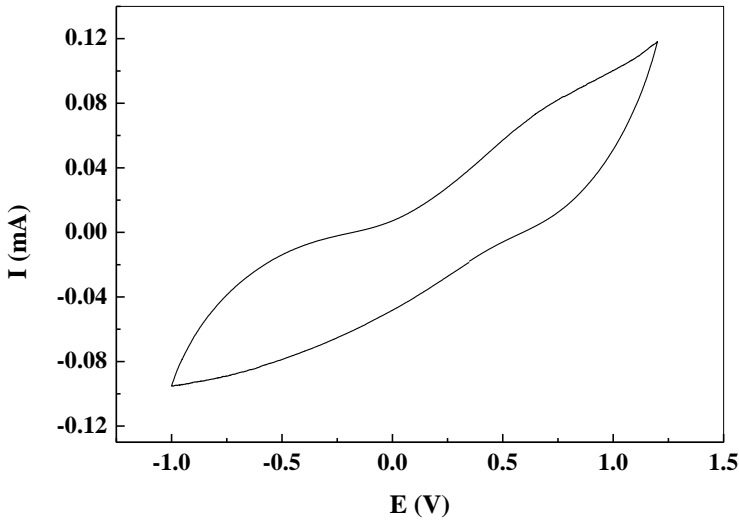


Figure 2. Electroactivity test of the deposited PPy film in a pyrrole-free solution.

3.2. Polymerization of pyrrole by chronoamperometry

In this section, we will study the formation of polypyrrole deposits by imposing a potential between the working electrode and the reference electrode.

The deposition potential that we have chosen from the cyclic voltammogram of figure 1 is 1.1 V, this potential allows continuous oxidation of the monomer on silicon.

We report in figure 3 the current evolution as a function of time recorded during the electrodeposition of PPy on silicon in potentiostatic mode. On the curve obtained, three main zones can be distinguished: after the double layer has been charged, the current density increases very rapidly and reaches a maximum value i_{\max} after a very short time ($t < 1$ s), this is attributed to the growth of a new phase and the increase in the number of nuclei formed on the electrode surface. Then, the current density gradually decreases with time to a steady state where it remains unchanged.

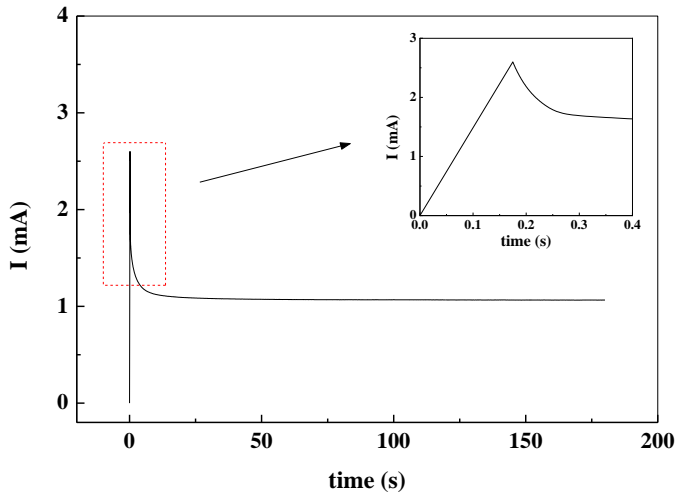


Figure 3. Current transient curve of PPy on Si. $E = 1.1$ V.

3.3. Electrosynthesis of PPy at different applied potentials

When potentiostatically depositing PPy, it is very important to carefully choose the applied potential, as this determines the amount of polymer that will be deposited, and then it determines the final characteristics of the polymer layer. In our study, we tested the effect of this crucial factor by imposing different constant potentials, from 0.9 to 1.2 V, and we followed the evolution of the current versus time. The curves obtained are shown in figure 4.

It can be seen that the curves obtained all have the same appearance. It is also observed that as the imposed potential increases, the current density i_{\max} increases, which influences the quantity of polymer deposited on the electrode surface.

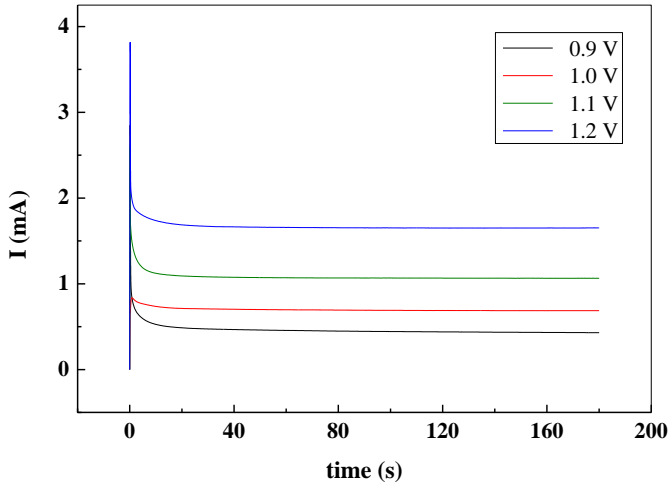


Figure 4. Electropolymerization of pyrrole on silicon electrode by the potentiostatic method at different imposed potentials.

3.4.Characterization of the PPy films obtained

The morphological characteristics of the obtained PPy film were examined by the atomic force microscope (AFM) and by scanning electron microscopy (SEM). As shown in Figure 5, the PPy layer covers the entire silicon surface. It has a relatively rough surface (RMS=108.263 nm).

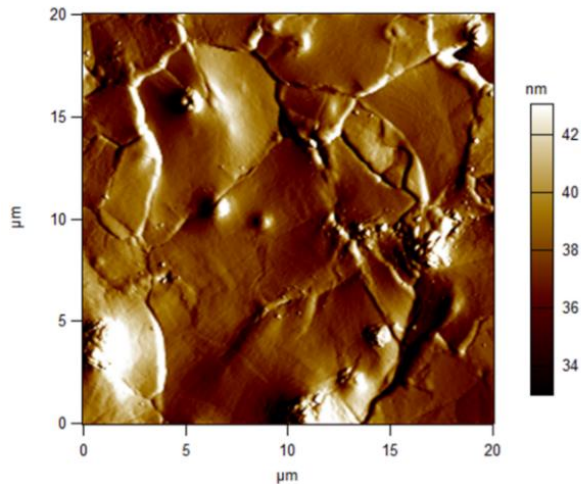


Figure 5. 2D AFM image of PPy film prepared at 1.1V.

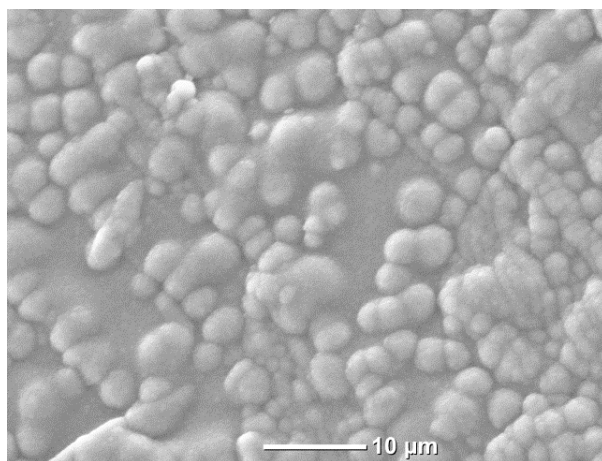


Figure 6. SEM image of the PPy film deposited on silicon at 1.1V.

The SEM micrograph of the polypyrrole film deposited on silicon using the potentiostatic mode (Figure 6) shows a homogeneous surface morphology characterized by a globular structure formed by homogeneous globules distributed over the entire surface of the deposit.

4. Conclusion

In this work, we electrochemically synthesized polypyrrole films onto silicon substrates by imposing an oxidation potential in an organic medium of pyrrole. Potentiostatic mode of electrodeposition leads to a well adhering homogeneous polypyrrole films on silicon supports. The structure of the as-formed film, as shown by SEM technique, represents a very promising support to receive a multitude of other phases, namely metallic particles, to prepare active materials.

References

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