

New Composite Electrode Material Based on Glassy Carbone/Polythiophene/MnO₂

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Abstract: In this paper, it presents the work which consists to develop and characterize a modified electrode with a conductive polymer film, poly [3-methyl thiophene] then incorporating manganese dioxide MnO₂ into the film. The deposition of the polymer film on the surface of the glassy carbon electrode is realized by the electrochemical oxidation of the monomer [3-methyl thiophene] in an organic medium. Then the electrode obtained was immersed in a solution containing ions Mn⁴⁺ to introduce into the polymeric film. The technique of insertion of manganese ions is performed by interaction with the polymer film. The electrochemical oxidation of the modified electrode in an aqueous medium will precipitate the manganese dioxide in the form of particles in the polymer film. In this study, it was found that several parameters affect the amount of manganese dioxide introduced as the pH of the medium and the thickness of the polymer film.

Key words: Modified electrodes, conductive polymer, polythiophene, manganese dioxide, energy storage.

1. Introduction

The urgent need for electric systems and devices that require power sources of high performance have stimulated the research areas related to energy storage. In addition, the increasing environmental and economic impact of the production and the use of fossil fuels have stimulated the search for alternative energy sources, such as electrochemical energy (batteries, fuel cells and electrochemical capacitors) [1]. In this regard, conventional capacitors and batteries are recognized as highly attractive energy storage devices to satisfy the above needs.

Composite materials composed of conductive polymers and inorganic particles have attracted considerable attention because they can combine the advantages of both components and have potential applications in many areas [2]. A variety of organic polymers and inorganic solids have been successfully combined to form nanocomposites structures [3-5].

Polythiophene is one of the promising conducting polymers for use in rechargeable batteries due to its high conductivity, high theoretical specific capacity, and low cost.

The electrochemical modification of electrode surface by polymer films containing metal particles is an effective method to prepare modified electrodes with specific electrocatalytic properties and orient the electrochemical properties of reactions occurring at the interface of these electrodes [6-8].

In this paper, we present our work which consists to develop and study a modified electrode with a conductive polymer film, poly [3-methyl thiophene] and to incorporate manganese dioxide MnO₂ in the film. We will study the influence of certain parameters on the amount of incorporated manganese dioxide.

2. Experiments

In our experience, the electrochemical study of manganese was carried out in two different environments. In aqueous media, the solvent used is distilled water and the sulphate sodium "Na₂SO₄" as

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supporting electrolyte. In an organic medium, the solvent used is acetonitrile, CH₃CN, and the supporting electrolyte is lithium perchlorate, LiClO₄. The reagents used are manganese sulphate, MnSO₄, 2H₂O and the monomer 3-methyl thiophene.

The apparatus used for the characterization of our modified electrode (cyclic voltammetry and coulometry) is VoltaLab 40 (PGZ 301) controlled by a voltamaster software of type radiometer to control the potential and record the electrical current.

The experiments were performed in a three electrode cell. The working electrode is a glassy carbon disk of 0.07 cm² (3 mm of diameter). It was polished with diamond preparation, and then rinsed with distilled water and dried with Joseph paper before each manipulation. The reference electrode on saturated calomel has a fixed and constant potential. The auxiliary electrode is an electrode with a stainless platinum wire.

3. Results and Discussion

3.1 Study of Electrochemical Behavior of Manganese (II) on a Glassy Carbon Electrode

The electrochemical behavior of manganese was studied on a glassy carbon electrode of 0.07 cm² surface by digital cyclic voltammetry in a solution of manganese (MnSO₄) 10⁻² M with 10⁻¹ M of Na₂SO₄.

The obtained curve on a potential range of -1.6-1.6 V/SCE is characterized by the presence of a weak oxidation peak around 0.310 V corresponding to the oxidation of manganese introduced in the reduction of ions of manganese (II) and a very intense peak at 1 V attributed to the formation of Mn⁴⁺ ions. At the return sweep we also observe two peaks in the vicinity of 0.780 V/SCE and 0.005 V/SCE corresponding to the reduction of Mn⁴⁺ species in Mn³⁺ and the Mn³⁺ in Mn²⁺, respectively (Fig. 1a).

Successive scans show an increase of peak intensity of reduction and oxidation. The increase in oxidation peaks is due to the modification of the electrode surface during the scans. The beginning of the oxidation peak in the vicinity of 0.8 V from the sixth cycle corresponds to the oxidation of Mn²⁺ to Mn³⁺ (Fig. 1b).

3.2 Electropolymerization of the Monomer (3-Methyl Thiophene)

The monomer 4 × 10⁻³ M was electropolymerized on glassy carbon by cyclic voltammetry in an organic medium of acetonitrile 0.1 M in lithium perchlorate.

The obtained curve (Fig. 2) shows the presence of an irreversible oxidation peak at 1.45 V corresponding to the oxidation (polymerization) of the monomer and therefore to the formation of poly [3-methyl thiophene]

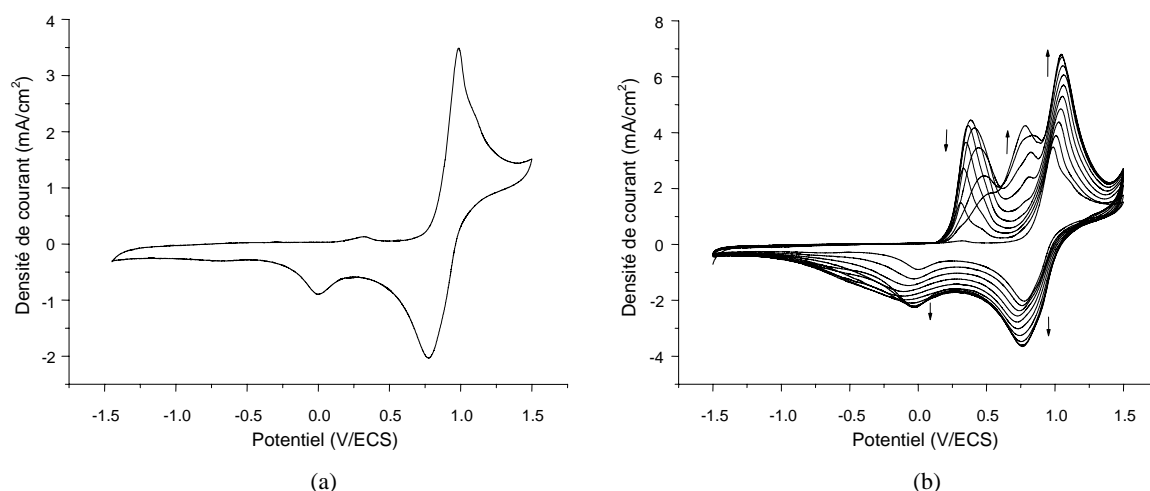


Fig. 1 Oxydo-reduction cyclic voltammograms Manganese (II) plotted on glassy carbon electrode in an aqueous solution 10⁻² M MnSO₄, at $\nu = 100$ mV/s. (a) first cycle and (b) successive scans (10 cycles).

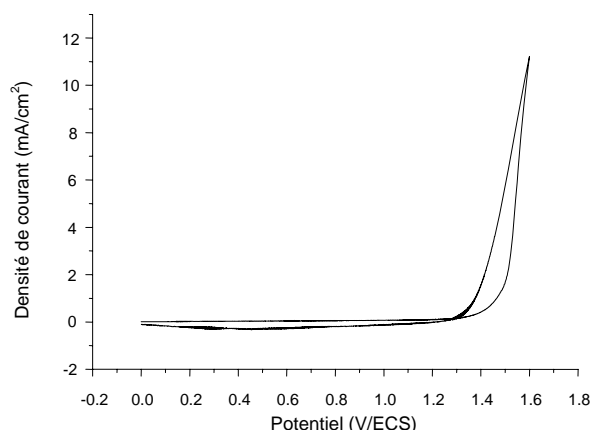


Fig. 2 Cyclic voltammetry curve of the monomer onto glassy carbon electrode ($S = 0.07 \text{ cm}^2$) in CH_3CN 0.1 M LiClO_4 and $4 \times 10^{-3} \text{ M}$ of 3-methyl thiophene, $\nu = 100 \text{ mV/s}$.

deposited on the electrode surface. In return, we see a reduction wave at 0.455 V corresponding to the reduction of the polymer film deposited on the electrode.

Successive scanning leads to the growth of the polymer film deposited on the electrode surface. This is confirmed by the electrochemical response which exhibits a reversible wave in the vicinity of 0.4-0.6 V, attributed to polythiophene (Fig. 3).

3.3 Incorporation of Manganese (IV) in the Polymer Film

In order to incorporate manganese dioxide in the polymer film, we deposited a poly [3-methyl thiophene] film on the surface of a glassy carbon electrode. The electrode thus modified is immersed in a solution of 10^{-2} M MnSO_4 for 10 min to allow the incorporation of Mn (II) by interactions. Then, the electrode was rinsed with distilled water for removing the excess of manganese (II) not associated with the polymer. A cyclic voltammetry was performed in a solution of 10^{-1} M Na_2SO_4 in the potential range between 400 and 1,600 mV at a scan speed $\nu = 10 \text{ mV/s}$ to show the formation of manganese dioxide in the polymer film. The curve obtained is characterized by an intense peak at 1.4 V corresponding to the oxidation of the incorporated Mn (II) in Mn (IV) onto the surface of the modified electrode (Fig. 4).

3.4 Influence of the Medium Concentration on the Amount of Incorporated Mn (II)

A glassy carbon electrode modified with a poly [3-methyl thiophene] film was immersed in solutions MnSO_4 of different concentrations for 10 min and then oxidized in 10^{-1} M Na_2SO_4 by cyclic voltammetry with a scanning speed $\nu = 10 \text{ mV/s}$.

The evolution of the quantity of incorporated manganese in function of the solution concentration is shown in Fig. 5. We note that the amount of

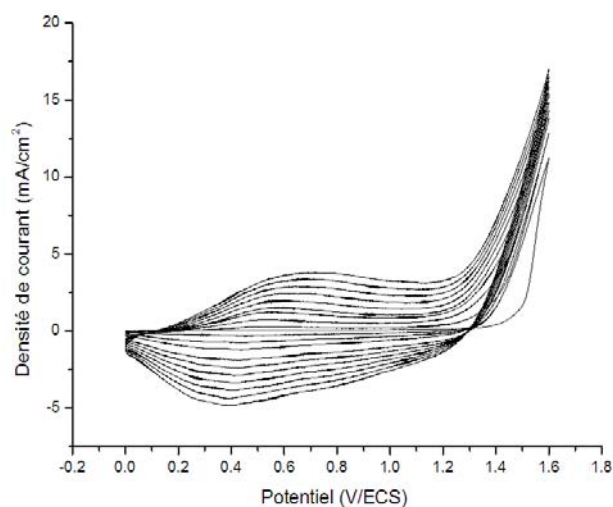


Fig. 3 Diagram of cyclic voltammetry of the electropolymerization of the monomer by successive scans on a glassy carbon electrode ($S = 0.07 \text{ cm}^2$) in CH_3CN with 0.1 M LiClO_4 and $4 \times 10^{-3} \text{ M}$ of monomer at $\nu = 100 \text{ mV/s}$.

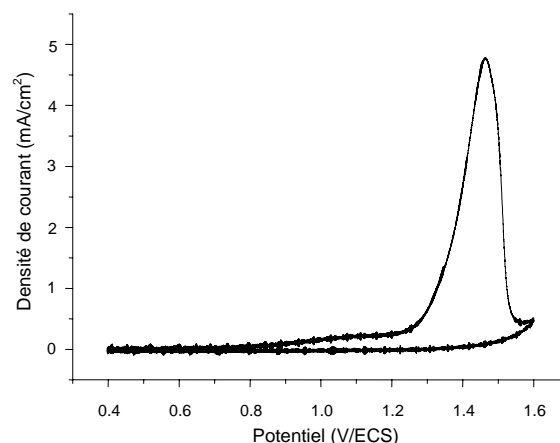


Fig. 4 Cyclic voltammetry diagram of Manganese (II) on glassy carbon electrode modified with a polymer film in an aqueous solution of Na_2SO_4 10^{-1} M for 10 min after immersion in a solution containing cations of Manganese (MnSO_4 10^{-2} M), at $\nu = 10 \text{ mV/s}$.

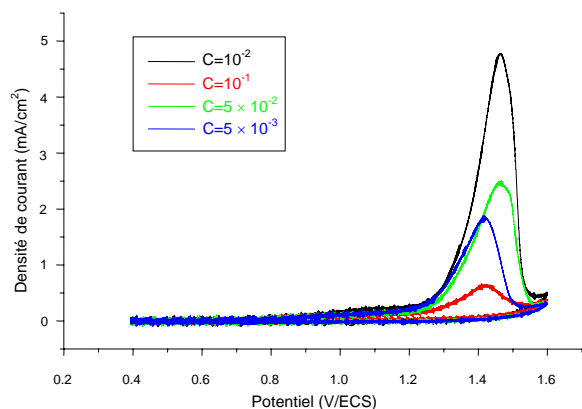


Fig. 5 Anodic oxidations curves of incorporated Manganese (II) in the polymer film in 10^{-1} M Na_2SO_4 after immersion of modified electrodes for 10 min at various concentrations, at $v = 10$ mV/s.

incorporated manganese varies with the concentration. It appears that the interaction between manganese cations and the polymer film depends on the concentration. The optimum incorporated amount is obtained for a concentration of 10^{-2} M.

3.5 Influence of Medium pH on the Amount of Incorporated Mn (II)

We varied the pH of the solution 10^{-2} M MnSO_4 to see its influence on the incorporation of manganese (II) in the polymer film deposited on the glassy carbon electrode. The modified electrode is immersed in the solution of MnSO_4 at different pH between 3.9 and 7 and then rinsed with distilled water to remove excess ions of manganese (II) not retained by the polymeric film. The electrode is then oxidized in an aqueous solution containing only the supporting electrolyte Na_2SO_4 10^{-1} M to oxidize manganese cations (II) retained in the film of manganese (IV) by cyclic voltammetry with a scan rate of 10 mV/s.

The voltammograms obtained at different pH are summarized in Fig. 6. We note that the current intensity of the oxidation peak varies with the medium pH; the amount incorporated is maximal at pH 5.27.

3.6 Effect of Thickness of Poly [3-Methyl Thiophene] Film

To see the effect of film thickness of poly [3-methyl

thiophene] on the amount of incorporated manganese, we passed, by coulometry, various charges: 5 mC, 10 mC and 15 mC for depositing layers of a polymer film of various thicknesses. These modified electrodes were then immersed for 10 min in a solution of 10^{-2} M MnSO_4 to allow the incorporation of manganese (II) in the film by interaction, and then oxidized in an aqueous solution containing Na_2SO_4 10^{-1} M by cyclic voltammetry at a scan rate of 10 mV/s.

We note that the intensity of the peak oxidation is more important for less thinner films (Fig. 7). The interactions between manganese cations and the

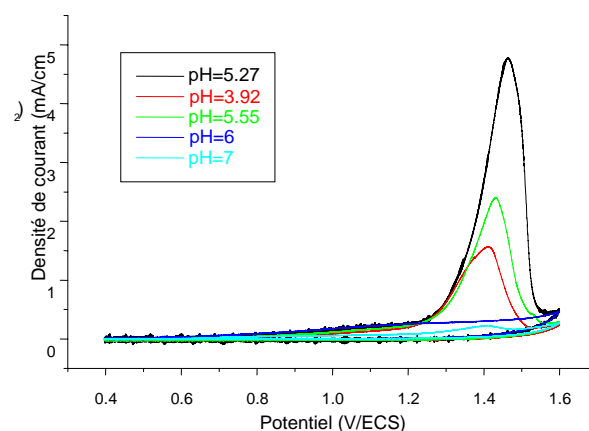


Fig. 6 Anodic oxidations curves of Manganese (II) deposited in the polymer film in 0.1 M Na_2SO_4 , after immersing the modified electrodes for 10 min in a solution of MnSO_4 10^{-2} M at different pH and at $v = 10$ mV/s.

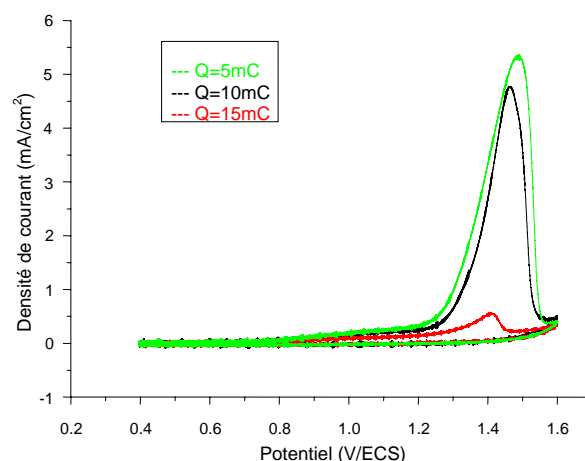


Fig. 7 Anodic oxidations curves in 10^{-1} M Na_2SO_4 Manganese (II) incorporated into the polymer film after immersion of modified electrodes for 10 min in a solution of MnSO_4 10^{-2} M at different thicknesses and at $v = 10$ mV/s.

polymer film depend on the film thickness. When the film is thick, the interactions decrease due to the non permeability of the polymer.

4. Conclusions

In this work, the film deposition of poly [3-methyl thiophene] to the surface of the glassy carbon electrode is done by the electrochemical oxidation of the monomer in an organic solution of acetonitrile. The inclusion of the manganese dioxide in the films of poly [3-methyl thiophene] is performed by immersion of the modified electrode in an aqueous solution containing manganese ions for incorporation in the polymeric film by interaction, followed by an electrooxidation to precipitate the manganese dioxide particles. The presence of manganese dioxide (Mn⁴⁺) in polymer films is confirmed by the presence of an oxidation peak of incorporated manganese.

We found that several parameters affect the amount of incorporated manganese dioxide such as the solution concentration, the medium pH and the thickness of the polymer film.

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