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

Imene Chikouche, Ali Sahari, Fahima Charef and Ahmed Zouaoui
Faculty of Technology, Ferhat Abbas University, Setif 19000, Algeria

Received: November 30, 2012 / Accepted: January 06, 2013 / Published: May 25, 2013.

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
supporting electrolyte. In an organic medium, the solvent used is acetonitrile, CH$_3$CN, and the supporting electrolyte is lithium perchlorate, LiClO$_4$. The reagents used are manganese sulphate, MnSO$_4$, 2H$_2$O 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 cm$^2$ (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 cm$^2$ surface by digital cyclic voltammetry in a solution of manganese (MnSO$_4$) 10$^{-2}$ M with 10$^{-1}$ M of Na$_2$SO$_4$. 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 Mn$^{4+}$ 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 Mn$^{4+}$ species in Mn$^{3+}$ and the Mn$^{3+}$ in Mn$^{2+}$, 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 Mn$^{2+}$ to Mn$^{3+}$ (Fig. 1b).

3.2 Electropolymerization of the Monomer (3-Methyl Thiophene)

The monomer 4 $\times$ 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]
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$_2$SO$_4$ in the potential range between 400 and 1,600 mV at a scan speed $v = 10$ 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$_2$SO$_4$ by cyclic voltammetry with a scanning speed $v = 10$ 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
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 MnSO₄ 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 MnSO₄ 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 Na₂SO₄ $10^{-1}$ 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 MnSO₄ to allow the incorporation of manganese (II) in the film by interaction, and then oxidized in an aqueous solution containing Na₂SO₄ $10^{-1}$ 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
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 (Mn$^{4+}$) 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.

References

[1] E.C. Rios, A.V. Rosario, R.M.Q. Mello, L. Micaroni, Poly(3-methylthiophene)/MnO$_2$ composite electrodes as electrochemical capacitors, Journal of Power Sources 163 (2007) 1137.
[2] X.X. Liu, L.J. Bian, L. Zhang, L.J. Zhang, Composite films of polyaniline and molybdenum oxide formed by electrocodeposition in aqueous media, J. Solid State Electrochem 11 (2007) 1279.
[3] A. Lerf, Intercalation compounds in layered host lattices: supramolecular chemistry in nanodimensions, Handbook of Nanostructured Materials and Nanotechnology, H. Nalwa, ed., Academic Press, New York 5 (2000) 1-166.
[4] S.J. Komarneni, Feature article: Nanocomposites, J. Mater. Chem. 2 (1992) 1219.
[5] Ozin, G. A.; Ozkar, S. AdV; Nanochemistry: Synthesis in diminishing dimensions, Mater. 4 (1992) 612.
[6] A. Zouaoui, O. Stéphan, M. Carrier, J.-C. Moutet, Electrodeposition of copper into functionalized polypyrrole films, J. Electroanal. Chem. 474 (1999) 113.
[7] J.C. Moutet, A. Zouaoui, Poly[(3-pyrrol-1-ylpropyl)malonic acid]: Synthesis, ion-exchange properties and complexation of copper cations, J. Electrochim. Acta 46 (2001) 4035.
[8] T. Melki, A. Zouaoui, B. Bendemagh, I.M.F. de Oliveira, G.F. de Oliveira, J.C. Lepêtre, et al., Electrosynthesis and catalytic activity of polymer-nickel particles composite electrode materials, J. Braz. Chem. Soc. 20 (8) (2009) 1523.