

REACTIVE POLYMERS ON ELECTRODES

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Abstract

The formation of conducting polymer films on electrodes by electropolymerisation of activated pyrrolic esters together with their characterisation is presented. Electrochemical evidence for the formation of by-layer polymer films is also reported. Modification of the films by reaction on the activated carbonyl esters is described.

Key Words: Poly(pyrrole), electropolymerisation, by-layer film, modified electrodes, post-polymerisation.

Introduction

Chemically modified electrodes by polymer films have been under intensive investigation due to their properties and potential applications [1]. Conducting polymers, such as poly(pyrrole), have been studied as films on electrodes. They can be easily obtained by electrochemical oxidation, are electroactive and can be switched between insulating and conducting states by electrochemical oxidation.

Solid phase reactions of conducting polymer films bound to electrodes possessing active esters were first reported by Pickett et al in 1994 [2]. It was shown that the film obtained after electropolymerisation of the pentafluorophenolate activated N-pyrrole was reactive and could undergo direct reactions with esters and amines to give new polymers with ester and amide functions.

Following previous work [3] we present results on the characterisation and reactivity of films obtained by electropolymerisation of two active pyrrolic ester monomers $C_4H_4NCH_2CH_2CO_2R$ [$R=C_6F_4-C_6F_5$ -(1); $2,4-(NO_2)_2C_6H_3$ -(2)]. Characterisation of the electroactive films formed on the electrode was made by cyclic voltammetry and coulometry, together with ex-situ diffuse reflectance FTIR spectroscopy (DRIFT). Reactivity of the polymer films was monitored by DRIFT and, in the case of poly (2), by UV-visible spectroscopy.

Results and discussion

Electropolymerization of the monomers **1** and **2** was carried out using 10 mM solutions of the monomer in MeCN - 0.1 M [NBu₄][BF₄], at Pt, Au and graphite disc electrodes, either by repetitive scan or at a fixed potential.

Figure 1 illustrates the growing of the film poly (1) with repetitive scans between 0.0 and 1.2 V vs. SCE. Care must be taken and higher potentials must be avoided in order to prevent over-oxidation and destruction of film conductivity. Figure 2 shows the cyclic voltammogram registered when the electrode modified by poly (2) is transferred to a cell containing only MeCN - 0.1 M [NBu₄][BF₄].

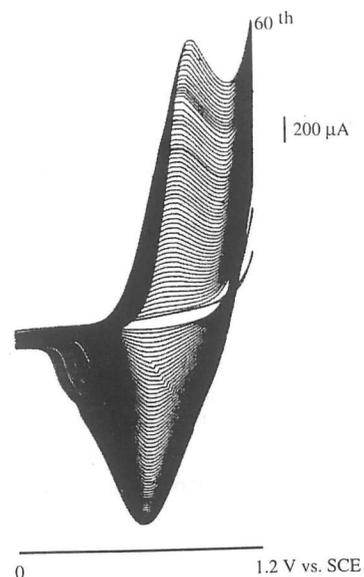


Figure 1 - Electropolymerisation, by repetitive scans between 0.0 and 1.2 V vs. SCE, of monomer 1 (10mM) in MeCN - 0.1 M [NBu₄][BF₄]. Pt electrode (A=0.64 cm²). Scan rate 0.10 V s⁻¹.

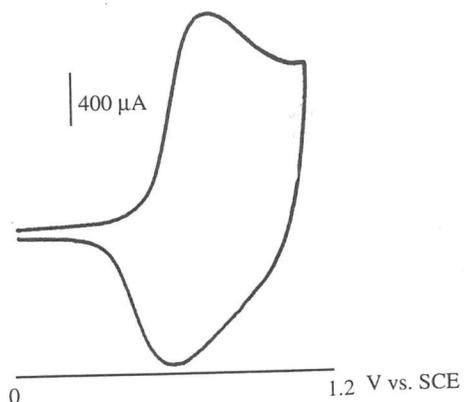


Figure 2 - Cyclic voltammogram at a Pt electrode modified by poly (2) in MeCN - 0.1 M [NBu₄][BF₄] solution. Scan rate 0.10 V s⁻¹.

Table 1 contains peak potential, charge, current efficiency, surface coverage and thickness data for the two films.

The values obtained for $E_{p^{ox}} + E_{p^{red}} / 2$ reflect the higher electron-withdrawing ability of the 4-(pentafluoro)tetrafluorophenyl group present in poly (1).

Table 1 - Peak potential, charge, current efficiency, surface coverage and thickness data for films poly (1) and poly (2).

| Polymer | $(E_{p^{ox}} + E_{p^{red}}) / 2$ (V vs. SCE) | Q_{growth} (mC) | Φ (%) | Γ (10 ⁻⁸ mol cm ⁻²) | δ (μ m) |
|----------|---|----------------------|---------------|--|------------------------|
| Poly (1) | 0.73 | 20 | 51 | 7.2 | 0.3 |
| | | 90 | | 32 | 1.2 |
| | | 300 | | 110 | 4.0 |
| Poly (2) | 0.66 | 10 | 44 | 3.8 | 0.08 |
| | | 90 | | 26 | 0.70 |
| | | 200 | | 64 | 1.60 |

Current efficiency, Φ , was calculated from a plot of Q^{ox} against Q_{growth} according to equation (1):

$$\Phi = (2.3 Q^{ox} / 0.3 Q_{growth}) 100 \% \quad (1)$$

where Q^{ox} is calculated from the area under the first quadrant, Q_{growth} is the charge consumed during electropolymerization measured coulometrically, 2.3 and 0.3 are the number of electrons transferred in the oxidation per unit of monomer and polymer, respectively [4].

Surface coverage of the films, Γ , was calculated from equation (2):

$$\Gamma = \Phi Q_{growth} / 2.3 F A 100 \quad (2)$$

where A is the electrode area in cm².

Thickness of the films, δ , was calculated from equation (3), assuming a cylindrical form:

$$\delta = \Phi M Q_{growth} / 2.3 F A d 100 \quad (3)$$

where F is the Faraday and the density, d, was assumed to be 1.2 g cm⁻³.

By-layer films of the type Pt/poly A/poly B were also constructed potentiostatically in two steps. In the first step a layer of poly (2) was grown ($E_{applied} = 1.06$ V vs. SCE; $Q_{growth} = 90$ mC) and the response of the modified Pt electrode in MeCN - 0.1 M [NBu₄][BF₄] is presented figure 3 a). The second step consisted on the potentiostatic growing of a second layer after the modified electrode was immersed in a 10 mM solution of a new monomer [R=3-NO₂C₆H₄-(3)] in MeCN - 0.1 M [NBu₄][BF₄] ($E_{applied} = 1.20$ V vs. SCE; $Q_{growth} = 90$ mC). As can be seen from figure 3 b) the charge, as calculated from the area under the wave, is approximately twice bigger.

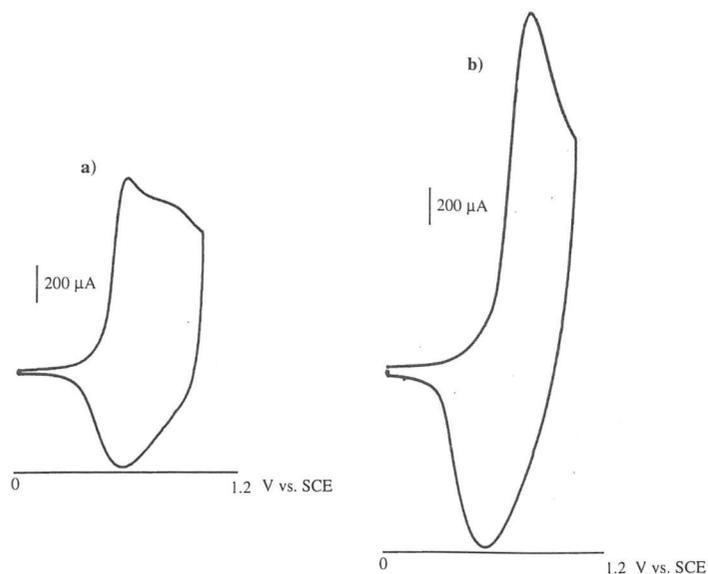


Figure 3 - Cyclic voltammograms in MeCN - 0.1 M [NBu₄][BF₄]. a) Pt electrode modified by poly(2); b) Pt electrode with a second layer of poly(3). Scan rate 0.10 V s⁻¹.

Ex-situ diffuse reflectance FTIR spectroscopy (DRIFT) recorded in the Kubelka-Munk mode was used to characterise the films obtained potentiostatically on Pt electrodes. As can be seen in figure 4 a) the spectrum of a film of poly (1) displays the bands characteristic of the groups present in the monomer, namely the bands at 1780 cm⁻¹ [ν(C=O)], 1503 cm⁻¹ [ν(C=C)_{ar}], 1121 cm⁻¹ [ν(C-O)] and 979 cm⁻¹ [ν(C-F)]. This shows that the monomer structure is kept after polymerisation.

Monitoring of the film reactions was possible using DRIFT. The spectra in figures 4 b) and c) were obtained when poly (1) was transferred to a MeOH - 0.1 M [NBu₄][BF₄] solution with triethylamine, at 22 °C. It can be observed a decrease, with time, of the bands associated with poly (1) and a simultaneous increase of a new band at 1740 cm⁻¹ due to the carbonyl methyl ester.

Similarly a film of poly (2) grown to ca. 1 μm, at 60 °C, undergoes complete conversion to the methyl ester within 30 minutes.

A new strategy was exploited for the construction of polymer films, based on post-polymerisation reactions. This can be illustrated for the methionine ester C₄H₄N(CH₂)₂CONHCH(CO₂CH₃)CH₂SCH₃. In fact, this compound could not be directly electropolymerised but the corresponding polymer could be built up on the electrode after reaction of poly (1) with the methionine methyl ester.

The film poly (2) turned out to be a very interesting starting material for the study of post-polymerisation reactions. The co-product, 2,4-dinitrophenol, liberated to the solution during reaction, absorbs in the UV-visible region. From the amount of 2,4-dinitrophenol released to the solution at the end of reaction (constant absorbance) the extension of the reaction was calculated.

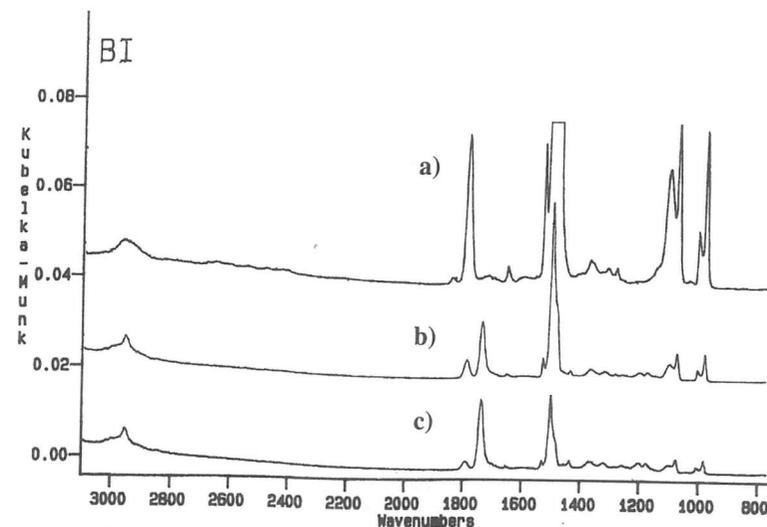


Figure 4 - DRIFT spectra of poly (1) before reaction (a); during reaction with methanol after 15 minutes (b) and 30 minutes (c).

From the graph in figure 5, where a linear correlation between the total amount of 2,4-dinitrophenol released and the thickness of the film is shown, it can be concluded that all the reactive material in poly (2) undergoes reaction independently of the film thickness. This means that all the reactive sites in poly(2) are accessible to reactants.

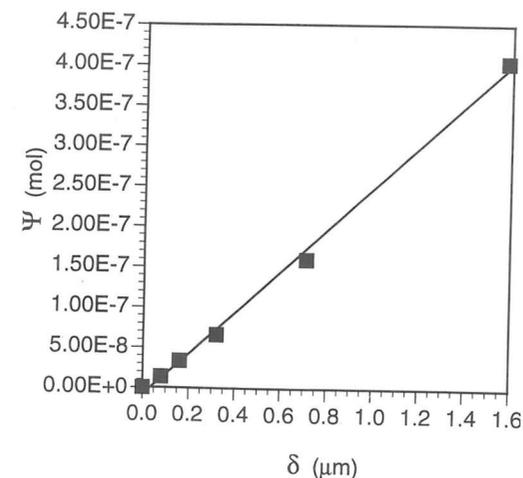


Figure 5 - Graph of the total amount of 2,4-dinitrophenol released (Ψ) against the thickness of the films.

From absorbance vs. time plots, reactions can be monitored. This method offers a new way for the calculation of the kinetic and thermodynamic parameters for the reaction.

Final Comment

Active pyrrolic ester films can be easily prepared by electrochemical oxidation with reasonable efficiencies that are independent of film thickness. They can be characterised by electrochemical and spectroscopic techniques. They undergo facile, high yield reactions, this opens new prospects for their modification and insertion of new active functions, namely amides that can not undergo direct electropolymerisation.

Acknowledgements

This work has been partially supported by JNICT. M Passos is grateful to INVOTAN for providing travel funds and to Dr. C Pickett for the facilities offered to work in the Nitrogen Fixation Laboratory at Norwich.

References

- 1 - A G MacDiarmid and A J Epstein, "Science and Applications of Conductive Polymers", W R Salaneck, D T Clark and E J Samuelson Ed., Adam Hilger, (1991) pp.117-127.
- 2 - C J Pickett and K S Ryder, *J C S Dalton Transactions*, (1994) 2181.
- 3 - M S Passos, M A Queirós, T Le Gall, S K Ibrahim and C J Pickett, *J Electroanal. Chem.*, in press.
- 4 - A F Diaz, J Castillo, K K Kanazawa, J A Logan, M Salmon and O Fajardo, *J Electroanal. Chem. Interfacial Electrochem.*, (1982) 133, 233.

A DC/AC STUDY OF THE OXIDE FILM ON NIOBIUM IN BORATE SOLUTIONS

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Abstract

This paper reports on the electrochemical characterisation of the oxide film grown on niobium in a borate buffer solution of pH 8.8 at room temperature. The formation of a duplex oxide, probably NbO_x ($x=1,2$) / Nb_2O_5 , is suggested by cyclic voltammetry results. Peak currents and scan rates showed a linear dependency when plotted in the log-log plane, exhibiting a unity slope indicating control by a surface process. Electrochemical impedance spectroscopy confirmed the voltammetry results. Impedance spectra were conducted within the potential domains of both anodic peaks after 10 cycles at 200 mVs^{-1} . Bode plot analysis and simulation by the equivalent circuit approach suggested an extra time constant when cycling was extended to include the second peak. The stability of the oxide film was tested in 0.5 M sodium chloride solutions at a low scan rate (0.2 mVs^{-1}) showing no breakdown up to 2500 mV (SCE).

Key words: niobium oxides, niobium, anodic oxidation, impedance spectroscopy.

Introduction

The motivation for this study lies on the excellent corrosion resistance of niobium and its oxides and also in the possibility of using it as a coating or as an element for superficial alloying. This is particularly attractive in the case of aluminium. In fact, in the last ten years, a variety of corrosion resistant aluminium alloys have been prepared by non-equilibrium alloying methods using Cr, Mo, Ta, W, Zr [1,2]. Results concerning Nb are somewhat scarce.

Most studies related to the formation of the anodic film on niobium use galvanostatic conditions for its growth [3,4]. Passivation behaviour is complex in nature. Films thicker than several nm are expected to behave as semiconductors with electronic states in the semiconductor participating in the electron-transfer reaction. The semiconducting properties of the film, which is an n-type semiconductor, have been studied by several authors [3-9].

This paper reports on preliminary results on the electrochemical characterisation of oxide film grown on niobium, under potentiodynamic control, in a borate solution of pH 8.8 at room temperature.

Experimental

The working electrode was a spectroscopically pure niobium rod with 3mm of diameter. The electrode was mounted in epoxy resin with a copper wire providing electrical contact. Experiments were run in a conventional three electrode cell (Greene cell). The secondary electrode was a helix of Pt wire and a saturated calomel electrode (SCE) was used as reference.