

Thin Layers of Polyaniline/TiO₂ Nano-particles Using Electrochemical Deposition

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Abstract: - By cycling voltammetry the thin layers of polyaniline on mechanically polished Nb electrode from sulfuric aqueous solutions with aniline added were deposited. During the repetitive voltammetric scans, by simultaneous in-situ Raman spectroscopical measurements, the redox reactions and formation of degradation products in polymer film were investigated. It was found that the new monitored voltammetric waves appear only when the polyaniline reaches an over-oxidized state. The comparative measurements on Pt electrode in sulfuric aqueous solutions with aniline and TiO₂ nano-particles added were also performed. It was shown that the TiO₂ nano-particles inhibits the formation of degradation products

Key-Words: - Polyaniline, TiO₂ nano particles, cyclic voltammetry, Raman spectroscopy

1 Introduction

The thin layers of polyaniline were intensively investigated as promising material for the development of organic semiconductors, colour displays, energy storage, devices, rechargeable polymer batteries etc. [1,2]. The electrochemical deposition of polyaniline using cyclic voltammetry is particularly useful for elucidating basic aspects of the polymer growth and redox mechanisms.

Conductivity of polyaniline strongly depends on the degree of oxidation and protonation of polymeric backbone. It varies over 10 orders of magnitude when the half oxidized form is fully protonated, passing from approx. 10^{-8} Scm^{-1} to 10^2 Scm^{-1} . The conductivity of electrodeposited polyaniline film can be changed very easy by variation of applied potential, during the cyclic voltammetry scans.

The reversibility of redox reactions in polymer film strongly depend on potential region, type of electrolyte, electrolyte concentrations, supporting electrodes, pre-treatment of the supporting electrode surfaces etc. During the cyclisation, if the anodic potential is higher than some limit potential, the polymer film pass in the over-oxidized state with formation of degradation products which diminish the reversibility of redox reactions [3].

The aim of this study is to enlarge the initially studied domain of electrochemical synthesis of polyaniline on some valve metals, and we report here some of our preliminary results for electro-

chemical response of polyaniline in presence of TiO₂ nano-particles

2 Problem Formulation

The polyaniline can be used as electrode material in rechargeable batteries if it has good reproducibility during the multiple charging discharging processes. The electrodeposited polymer film can be more applicable if the potential range is larger and if the number of repetitive cycles of redox reactions without appearance of degradation products is bigger. For most used supporting electrodes prepared from noble metals (Pt, Au) and inert substrates (graphite, glassy carbon, ITO etc.) the potential region of repetitive cyclic voltammetry scans is limited from -0.2 to 0.7 V (SCE) . The main problems is to find some supporting electrode that, during the cyclic voltammetry scans will allow to widen the potential range and also to produce homogeneous electrodeposited thin layers.

3 Problem Solution

The introduction of valve metals (Nb, Ti, Ta) into polymer electrochemistry give the possibility to widen the potential range and to obtain new electrochemical data for existing redox reactions and degradation products in polymer film [4].

On fig.1. typical voltammograms on mechanically polished Nb electrode in 1M H₂SO₄ for the wider cathodic potential of -0.75 V SCE without apparition of significant cathodic current, i.e. hydrogen evolution are presented. The first cycle always shows active region followed by a large current plateau of a passive region. On the reverse sweep the reduction of the formed passive film is not present, i.e. the formed passive film becomes chemically and electrochemically stable. The passivity of electrode is a result of formation of a protective oxide film whose thickness grown with applied anodic potential. After the first cycle the Nb electrode remained passive in the all investigated potential regions.

In the second cycle the formed passive film blocked all possible redox reactions in the interface Nb/passive film/electrolyte. In the next cycles, the voltammograms have similar shapes as voltammogram 2 on fig.1, i.e. the Nb electrode becomes electrochemically "inert". In such electrode is possible to study electro-deposition of polymer films because all variations of current density during the sweeps will depend only of deposition processes and redox reactions in polymer film.

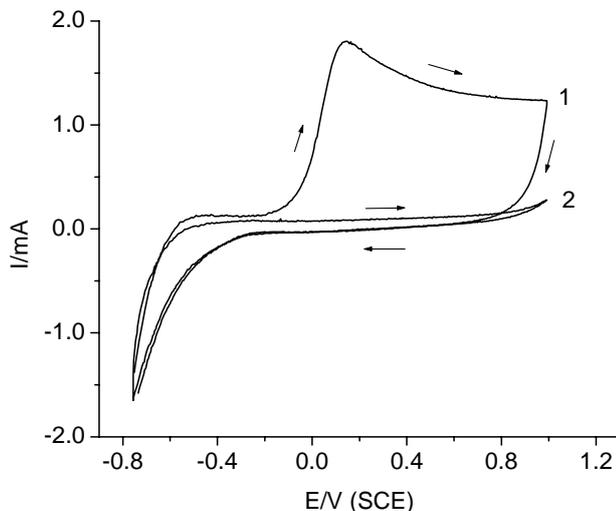


Fig.1. Voltammograms of Nb electrode immersed in 1 M H₂SO₄ ($v = 200$ mV/s), 1 and 2 represent number of cycles

Fig.2. shows cyclic voltammograms recorded on mechanically polished Nb electrode in aqueous sulfuric acid solution with aniline added, for the potential region between -0.6 and 0.9 V (SCE). The cyclic potential was repeated 33 times on the same electrode. For clarity, on fig.2. only the voltammograms from 24 to 33 cycles are shown. During every cycle the electrodeposited film thickness grows

successively and the anodic and cathodic peaks rise in intensity.

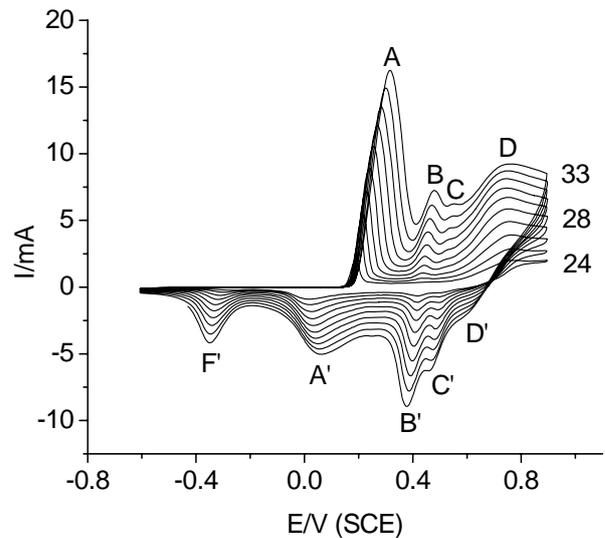


Fig.2. Voltammograms of Nb electrode recorded after multicyle scans in 1 M H₂SO₄ + 0.1 M aniline. ($v = 20$ mV/s).

The multiple redox peaks on fig.2. indicate the complexity of the redox processes, involving coupled electron transfer reactions

Peaks D-D', located at most positive potentials on the voltammograms, only appear for limit anodic potentials higher than 0.75 V (SCE) and slow scan rate. For faster scan rate these peaks begin to rise in intensity after about 50 cycles. But, for limit anodic potential of 0.9 V (SCE) these peaks appear after a few cycles.

The middle peaks B-B' and C-C' begin to appear only when the limit anodic potential on fig.2 reaches the value of peak D. These middle peaks have been attributed to the oxidation and reduction of the degradation products. For lower limit anodic potentials of electro-deposition, for instance at 0.6 V (SCE), polyaniline film exhibits a single pair of redox peaks A-A' and has a different structure from that of polyniline prepared at higher anodic potentials [3]. For limit anodic potential of 0.6 V (SCE) and faster sweep rate than 20 mV/s, the potential position of redox peaks A-A' doesn't shift even after 300 cycles, which confirms reversible redox reactions independent of the thickness of the film.

In voltammograms on fig.2. for the first time the cathodic peak F' is monitored on Nb electrode for potentials more negative than -0.2 V (SCE). The corresponding anodic peak F is merged in more intensive anodic peaks A, that was confirmed after the deconvolution of peak A.

The Raman spectroscopical measurements before and after each redox peak confirm that the appearance on new redox peaks F-F' is closely related to the so called "middle peaks" B-B' and C-C'. During the scan from -0.15 to -0.6 V (SCE) the difference between the Raman spectra confirmed the transition of the semi-quinoid and quinoid parts as well as polaronic part of benzene to para-disubstituted benzene rings. The redox wave A-A' correspond to the removal of electrons from nitrogen atoms of the amine between the benzene rings. For over-oxidized form of polyaniline film the degradation products were assigned as: benzoquinone, aminophenol, hydroquinone and quinoneimine.

For reducing the formation of degradation products, which diminish the reversibility of redox reactions, our next measurements were performed on Pt electrode introducing the TiO₂ nano-particles in polymer matrix.

On fig.3. the comparative voltammograms of polyaniline films with and without polymer coated nano-particles of TiO₂ deposited on electrode surface are shown.

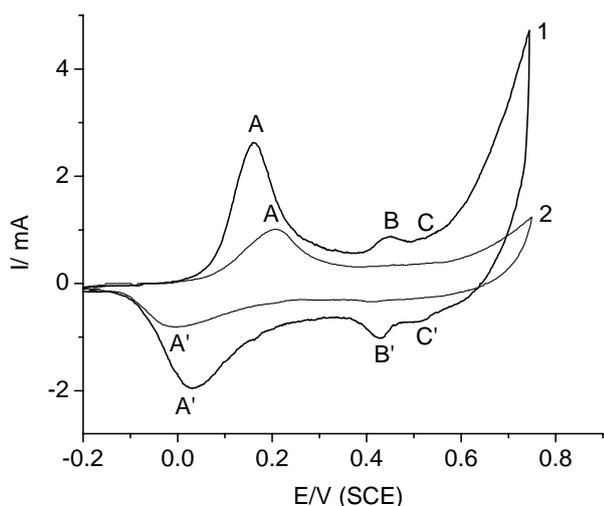


Fig.3. Comparative cyclic voltammograms recorded on Pt electrode in the aqueous solutions consisting of: 1 - 1 M H₂SO₄ + 0.1 M aniline, 2 - 1 M H₂SO₄ + 0.1 M aniline + 0.01 M TiO₂. ($v = 20$ mV/s)

As it can see from fig.3. the formation of new electrodeposited material (voltammogram 2) on the base of polyaniline/TiO₂ nano-particles is indicated by shifting of anodic peak A towards anodic direction and cathodic peak A' towards cathodic direction. The middle peaks B-B' and C-C' are missed indicating that the formation of degradation products in polymer film are inhibited.

Taking into account that the values of the redox charges under current peaks A and A' for polyaniline

/TiO₂ film (voltammogram 2) are quite smaller in intensity than under the peaks A and A' for polyaniline, at the moment is not clear if the polyaniline film is thicker than polyaniline/TiO₂ obtained in the same electrochemical conditions, or the presence of TiO₂ nano-particles decrease the electro-conductivity of the film.

Studies of the polyaniline/TiO₂ films electrodeposited on Nb electrode, as well as ellipsometric study of film thickness grows are in progress [5].

4 Conclusion

The mechanically polished Nb surfaces are very suitable for the electrochemical synthesis of polyaniline and study the mechanism of formation the degradation products into the polymer films. On Nb electrode it is possible to widen cathodic potential than usually applied on conventional electrodes.

For cathodic potentials more negative than -0.2 V SCE, the new redox peaks F-F' which are in close relation with middle peaks B-B' and C-C' were detected.

The electro-deposition of polyaniline and polyaniline/TiO₂ on Pt and Nb electrodes occurs approximately on the same oxidative potential of 0.7 V SCE. The presence of TiO₂ nano-particles inhibits the formation of degradation products in polymer film. These products are soluble in electrolytic solution and peel off from electrode surface, increasing irreversibility of redox processes.

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