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ELECTROCHEMICAL POLYMERIZATION OF ANILINE IN PRESENCE OF TiO_2 NANOPARTICLES

Irena Mickova, Abdurauf Prusi, Toma Grčev, Ljubomir Arsov*

Faculty of Technology and Metallurgy, Ss Cyril and Methodius University,
P. O. Box 580, MK-1001 Skopje, Republic of Macedonia
*arsov@tmf.ukim.edu.mk

The electrochemical polymerization of aniline from acid aqueous solutions of 1 M H_2SO_4 in presence of TiO_2 nanoparticles was performed by cyclic voltammetry. The heterogeneous polymerization of new synthesized materials from aniline monomers and electrodeposited TiO_2 polymer coated nanoparticles was analyzed using electrochemical techniques. During the repetitive cyclic voltammetry scans the presence of TiO_2 nanoparticles inhibits the polymer – related oxidation process and diminishes the degradation products in the composite materials. Good adhesion of composite materials on the Pt electrode, with superior electro-active repetitive properties in relation with pure polyaniline, was demonstrated.

Key words: polyaniline; TiO_2 nanoparticles; cyclic voltammetry

ЕЛЕКТРОХЕМИСКА ПОЛИМЕРИЗАЦИЈА НА АНИЛИН ВО ПРИСУСТВО НА НАНОЧЕСТИЧКИ ОД TiO_2

Со помош на циклична волтаметрија е испитувана електрохемиската полимеризација на анилин во кисели водни раствори во присуство на наночестички од TiO_2. Преку хетерогена полимеризација е синтетизиран нов композитен материјал од анилински мономери и електродепозитирани наночестички од TiO_2. Во текот на повеќекратна циклизација присуството на наночестички од TiO_2 ја инхибира реакцијата на оксидационата полимеризација, што условува намалување на деградациони продукти во композитниот материјал. Покажана е добра атхезивност на композитниот материјал врз Pt-електродата, како и негови супериорни електроактивни својства во однос на полианилинот.

Клучни зборови: полианилин; наночестички од TiO_2; циклична волтаметрија

INTRODUCTION

In scientific terminology the term “nanomaterials” refers to substances consisting of particles with dimensions in the order of 10^{-9} m (1 nanometer). The novel materials at the nanolevel exhibit new phenomena and characteristics, most of which we just now begin to explore and understand. The size scale, aspect ratio, and properties of nanomaterials provide advantages in a variety of applications, including electro-statically dissipative materials; advanced materials with combined stiffness and strength, as well as automotive components with enhanced mechanical properties [1–3].

Polyaniline is electro-conducting polymer containing a system of conjugated double bonds, and its properties combine semiconducting and metal physics with the molecular and solid-state chemistry. To make this polymer electrically conductive it is necessary to introduce mobile charge carriers. This can be done by oxidation or reduction reactions, commonly called ”doping” and “dedoping”, respectively, which can be performed by different chemical or electrochemical processing. Chemical doping-dedoping occurs when the polymer is exposed to an oxidizing or reducing agent, whereas electrochemical doping-dedoping can be obtained by anodic and cathodic polarization in suitable electrolytes [4–6].

The nanostructured metal oxides are promising new materials for blending with polymers for obtaining low weight nanocomposites with excellent mechanical, electrical, thermal, and multifunctional properties. The creation of nanocomposites based on electro-conductive polymers and nanostructured metal oxides, i.e. incorporation of inorganic filler into polymer matrixes, can dramatically improve their processibility [7–9].

The main goal in this work is to enlarge the existing knowledge of the preparation of new advanced materials consisting of polymer matrix with nanoparticles. The polymerization of aniline in presence of TiO_2 nanoparticles was performed by cyclic voltammetry. Comparative analysis of the resulting voltammograms with and without of TiO_2 demonstrated the creation of new composite material.

EXPERIMENTAL

Electrodes. Pt disc with an area of 24 mm^2, sealed in glass, was used as a working electrode. The electrode surface was machined flat and polished to a final smoothness of around 0.1 μm on successively finer grades of alumina powder lubricated with distilled water. Than, the electrode was cleaned in an ultrasonic bath and rinsed with ethanol. After each measurement the electrodeposited film was chemically dissolved in concentrated HNO_3.

The counter electrode was a Pt coil with a large surface; the reference electrode was a saturated calomel electrode (SCE). All potentials presented in this work refer to the SCE reference electrode.

Electrolytic cell. The electrolytic cell was classical three compartments cell. The working electrode was separated from the counter electrode by a fine porosity fritted glass disc and from the reference electrode by a Luggin capillary. The solution in the cell was purged by argon for at least 15 min prior to the start of each experiment. In every set of experiments, a new electrolyte was used to avoid the influence of possibly formed soluble species and olygomers.

Solutions and chemicals. Aqueous solutions of 1 M H_2SO_4 and 0.1 M aniline were prepared with triply distilled water. Prior to use aniline (Merck p.a.) was distilled to eliminate oxidized impurities and stored in the dark place under an argon atmosphere. Sulfuric acid (Merck p.a. 98 %) was used as received. Commercially pure TiO_2 nanoparticles with size of 21 nm were used as received. The suspension of 0.01 M TiO_2 nanoparticles was prepared in 1 M H_2SO_4 by vigorous stirring for two hours. The final solution consisting of 1 M H_2SO_4, 0.1 M aniline and 0.01 M TiO_2, was ultrasonically treated before the measurements in order to destroy potential agglomerates of TiO_2 particles in the solution.

Apparatus. The electrochemical measurements were carried out with a HEKA Model 488 potentiostat/galvanostat interfaced with a PC.

RESULTS AND DISCUSSION

The general formula for ideal polyaniline (PANI) materials in their base forms consists of three benzenoid ($–C_6NH_4–NH–$) units denoted B and one quinoid ($–N=C_6H_4=N–C_6H_4$) unit denoted Q, so that they can be written as $[(B–B)_y(Q–B)_{1–y}]_n$. The y value accounts to the oxidation state of the polymer: leucoemeraldine (completely reduced, $y = 1$), emeraldine salt (half reduced, $y = 0.5$) and pernigraniline salt (completely oxidized, $y = 0$) states [10–12].

In order to determine all existing redox reactions during the electrochemical polymerization and film deposition, cyclic voltammetry measurements were first performed in one larger potential region, starting from cathodic potential of –0.4 V (when hydrogen evolution on electrode surface occurs), up to +1 V (when degradation products in polymer film begin to be formed) [13–14]. Fig. 1 shows typical voltammograms recorded during the continuously applied cyclic voltammetric scans on the virgin Pt electrode immersed in aqueous solutions of H_2SO_4 containing aniline and TiO_2 nanoparticles.

As it can see from Fig. 1, in each forward scan 5 anodic and in each reverse scan 4 cathodic peaks appear. The intensity of the current in the anodic peaks; A, B, C and D, as well as in cathodic peaks A1, B1, C1 and D1 increases in each next cycle as a result of regular growth of polymer film on electrode surface. The voltammogram shapes are similar to the voltammogrames obtained during the electro-polymerization of polyaniline without presence of nanoparticles, reported in our previous works [15].

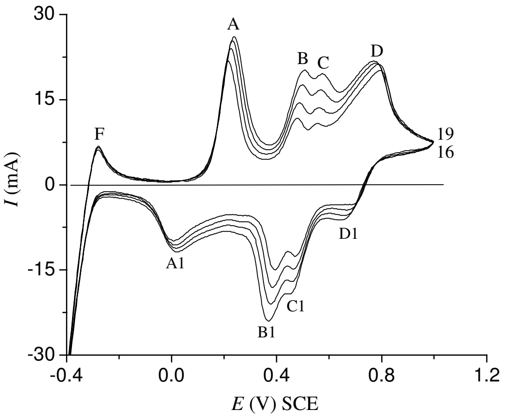

Fig. 1. Cyclic voltammograms from16 to 19 cycle registered on Pt electrode in solution consisting 1 M H_2SO_4 + 0.1 M anilin + 0.01 M TiO_2 (v = 5 mV/s)

The only difference is the smaller intensity of the current peaks, especially of the redox peaks B/B1 and C/C1, that can be associated with the degradation products in the polymer matrix. The 4 redox peaks are assigned as: A/A1 – semiquinone radical cations, i.e. polaron states of PANI (0/+1), B/B1 – benzoquinone/hydra-quinone, C/C1 – p-aminophenol/quinoneimine, and D/D1 – quinoid diradical dications, i.e. bipolaron state of PANI (+1/+2) [15]. The anodic peak F has the same intensity in each repetitive cycle and it originates from desorbed hydrogen that is beeing accumulated on the electrode surface during the cathodic polarization.

In literature data some controversy still exist over the interpretation of the middle peaks B/B1 and C/C1 in PANI films [16,17]. They also appear when the cyclic voltammetry measurements were performed with higher anodic potential limits through the redox peaks D/D1. For anodic potentials before the appearance of the anodic peak D, the only redox process on electrode surface is characterized with the redox peaks A/A1. The potential position of these redox peaks doesn't shift with increasing cycle number, even after 500 cycles, confirming the repetition of the reversible redox reactions independent on the thickness of the film. When the redox peaks D/D1 are reached, the degradation of PANI films begin. For limit anodic potentials that are more positive then the redox peaks D/D1, the middle peaks B/B1 and C/C1 gradually grow and in each next cycle the irreversibility of redox reactions increase. This is manifested by gradually shifting the peaks A and D towards anodic and peaks A1 and D1 towards cathodic direction. The degradation products manifested by peaks B/B1 and C/C1 are soluble in aqueous solutions and the formed PANI film begin to peel off from electrode surface.

The PANI films can be more applicable and effective if the potential range of anodic and cathodic polarization is larger, and if the number of repetitive cycles of redox reactions without appearance of degradation products is bigger. These conditions can be achieved by introducing the nanoparticles in polymer matrix that will form composite polymer materials, diminishing the possibility of formation of degradation products.

Shown in Figs 2 and 3 are comparative voltammograms of PANI films, with and without polymer coated nanoparticles of TiO_2 deposited on electrode surface, for two different values of cyclization rate.

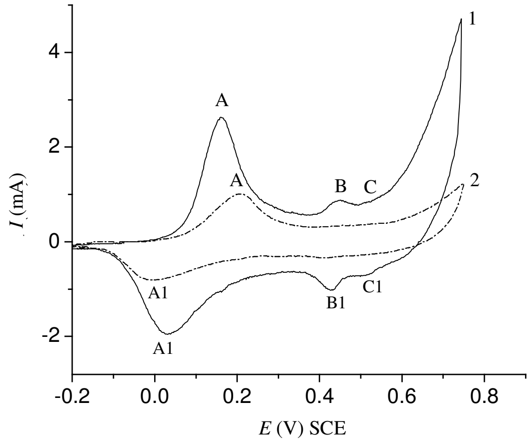

Fig. 2. Cyclic voltammograms of 8-th cycle registered on Pt electrode in the solution of: 1) 1 M H_2SO_4 + 0.1 M aniline; 2) 1 M H_2SO_4 + 0.1 M aniline + 0.01 M TiO_2 (v = 20 mV/s)

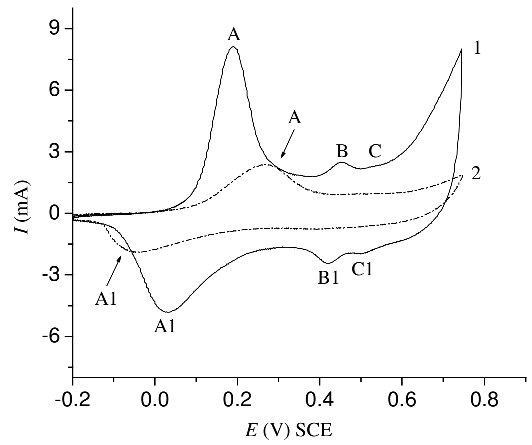

Fig. 3. Cyclic voltammograms of 8-th cycle registered on Pt electrode in the solution of: 1) 1 M H_2SO_4 + 0.1 M aniline; 2) 1 M H_2SO_4 + 0.1 M aniline + 0.01 M TiO_2 (v = 50 mV/s)

In both diagrams the formation of new composite materials on the base of PANI/TiO_2 is indicated by shifting of the anodic peak A toward the anodic direction, and the cathodic peak A1 toward the cathodic direction. These shifts are more pronounced for faster sweep rates, indicating notable change in electrochemical behavior of newly synthesized composite materials.

Taking into account the values of the redox-charges under current peaks A and A1 for both PANI films and PANI/TiO_2 composite materials (Fig. 2. and Fig. 3.), it can be concluded that the PANI films are much thicker comparing with PANI/TiO_2. The presence of TiO_2 nanoparticles in the composite films decrease the electrical conductivity of the film resulting in a strong increase on the peaks separation potential of the redox couple A/A1. In addition, the redox couples B/B1 and C/C1 of degradation products are inhibited, which is the main advantages of the composite film.

Shown in Fig. 4 is the separation potential of the redox couple A/A1, for both the PANI films and PANI/TiO_2 composite films, as a function of the sweep rate.

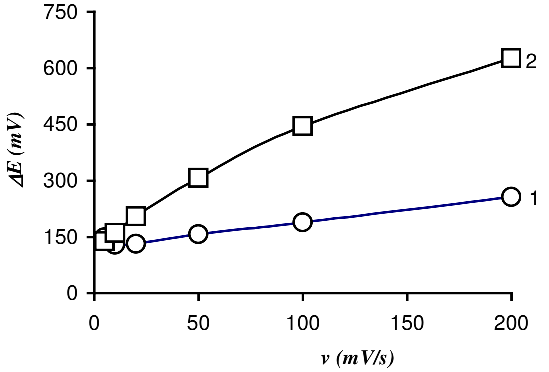

Fig. 4. Dependence of potential difference between peaks A and A1 of sweep rate in solution of: 1) 1 M H_2SO_4 + 0.1 M aniline; 2) 1M H_2SO_4 + 0.1 M aniline + 0.01 M TiO_2

According to the Nernst equation,

$$\Delta E = E_A - E_C = \frac{59}{n} \text{ (mV)}$$

during the cyclisation, for reversible redox processes the separation potential ΔE between anodic and cathodic peaks should be the same for all sweep rate. For irreversible redox processes, as the sweep rate is increased, the rate of mass transport increases and becomes comparable to the rate of electron transfer. The most noticeable effect of this process is the increase of the potential of peak separation ΔE. As it can seen in Fig. 4, the separation potentials between anodic and cathodic peaks in both cases increased with the sweep rate, but these increases are more pronounced in composite PANI/TiO_2 than in PANI films. It is evident that the irreversibility of redox couple A/A1 in PANI/TiO_2 composite films is higher than in PANI films.

Table 1 lists some characteristic electrochemical parameters, for various sweep rate, taken from registered voltammograms.

Table 1

Current intensities in cathodic and anodic peaks for various values of sweep rate registered on Pt electrode

		1 M H_2SO_4 + 0.1 M aniline			1 M H_2SO_4 + 0.1 M aniline + 0.01 M TiO_2		
v (mV/s)	$v^{1/2}$ (mV/s)$^{1/2}$	I_A (mA)	I_C (mA)	I_A/I_C	I_A (mA)	I_C (mA)	I_A/I_C
5	2.23	0.21	–0.22	0.95	0.15	–0.15	1.00
10	3.16	0.82	–0.79	1.03	0.42	–0.37	1.13
20	4.47	2.57	–1.93	1.36	1.00	–0.78	1.28
50	7.07	7.48	–5.15	1.45	2.26	–1.90	1.18
100	10.00	14.8	–10.4	1.42	3.80	–3.48	1.09
200	14.14	26.1	–19.6	1.33	6.11	–5.93	1.03

v – sweep rate, I_A – anodic current, I_C – cathodic current

From these values, it can concluded that the current peaks for redox couple A/A1 are much lower in the case of PANI/TiO_2 composite films, indicating that appreciably less quantity of electro active PANI species are present in this film. Analyzing the current peaks I_A and I_C as a function of sweep rate, (plots: $I_A - v$ and $I_C - v$, as well as $I_A - v^{1/2}$ and $I_C - v^{1/2}$), clearly show a better linearity of current peaks I_A and I_C vs v than the current peaks I_A and I_C vs $v^{1/2}$. Such a behavior indicates that the slowest step in the redox processes is diffusion of ions in the polymer films. This conclusion is in accordance with many literature results where the diffusion constants of ions in various electro-conducting polymer films is in order from 10^{-9} to 10^{-10} cm^2/s, and for diffusion of ions in electrolytic solutions, in order from 10^{-5} cm^2/s [7, 8, 18]. In addition, the calculated values of redox charges (under current peaks A and A1) for doppimg and dedopping processes were determined as ~55 mF/cm^2 (for PANI films), and ~20 mF/cm^2 (for PANI/TiO_2 composite films).

Taking into account that the usual values for redox capacitance of electro-conductive polymer films are mainly located in the region from 300 – 400 F/g, or 50 – 65 Ah/kg, for PANI with an approximately density of $\rho \approx$ 1.6 g/cm^3, the polymer film thickness in Fig. 2, after 8 cycles, can be estimated to be approximately 2 μm. The polymer thickness of PANI/TiO_2 composite films is much lower, but for more precise determination of this value the additional investigations, especially the density of composite material, are needed.

Concerning the reversibility/irreversibility of the redox couple A/A1 in both films (PANI and PANI/TiO_2), the diagnostic tests showed existence of quasi-reversible systems. For reversible processes: $\Delta E = 59/n$ (mV), the position of peaks potential are independent of sweep rate, and the ratio $(I_A/I_C) = 1$ and I_A and I_C are proportional with $v^{1/2}$. For totally irreversible processes there is no appearance of reverse peaks and for quasi reversible processes, I_A and I_C increase with $v^{1/2}$, but are not proportional to it, ΔE is greater than 59/n (mV) and increases with increasing v, the ratio $(I_A/I_C) = 1$, provided $\alpha_A = \alpha_C = 0.5$, and the potential position of the cathodic peak E_C shifts negatively with increasing v. In our case, all diagnostic tests for both PANI and PANI/TiO_2 films fit well to quasi-reversible systems. In addition, for all investigated sweep rates, the current ratios (I_A/I_C) of PANI/TiO_2 composite films are close to 1, indicating approximately equal transfer coefficients α of anodic α_A and cathodic α_C processes.

CONCLUSIONS

From comparative cyclic voltammetry measurements on Pt electrode in electrolytes consisting of 1 M H_2SO_4 + 0.1 M aniline and 1 M H_2SO_4 + 0.1 M anilin + 0.01 M TiO_2, the following conclusions can be drawn.

– The electrodeposition of PANI and PANI with TiO_2 nanoparticles occurs in the same potential range, approximately 0.7 V (SCE).

The presence of TiO_2 nanoparticles inhibits the polymer-related oxidation process and the characteristic redox peaks for PANI significantly diminish in intensity and shift from primary potential positions. The oxidation peaks A shift towards anodic and reduction A1 towards cathodic direction. These separations of peaks potential are larger for faster sweep rate indicating that the building of composite materials is a complex process depending of many parameters. The most important parameters are: diffusion of the TiO_2 nanoparticles from electrolyte solution to electrode surface, their migration in the polymer backbone during the film thickness growth (number of performed scans), and charge transfer in the polymer chain depending on existing energetic barriers provoked by TiO_2 nanoparticles.

– The redox processes in both PANI films and PANI/TiO_2 composite films are quasi reversible. The irreversibility of PANI/TiO_2 composite films are higher because the nanoparticles of TiO_2 decreased the electrical conductivity of the composite film.

– Studies of the mechanism for incorporation of metal-oxide nanoparticles in polymer backbone and formation of composite (PANI/TiO_2) composite materials are in progress.

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