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Electrocatalytic properties of the polypyrrole/magnetite hybrid modified electrode towards the reduction of hydrogen peroxide in the presence of dissolved oxygen

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ABSTRACT

In this study, we report on the electrocatalytic behaviour of a polypyrrole/magnetite hybrid electrode towards the reduction of hydrogen peroxide. The electrocatalytic activity of the composite electrode was demonstrated by cyclic voltammetric and chrono-amperometric measurements in comparison with the identically prepared neat polymer film. The stationary reduction currents, measured at an appropriately chosen potential (here at $E = -0.3$ V), plotted against the peroxide concentration gave a perfect linear correlation in nitrogen atmosphere in the micromolar concentration range. The performance of the composite electrode was not affected by the presence of sulphate, nitrate or chloride anions. In the presence of dissolved oxygen a complex electrocatalytic activity was observed, involving the reduction of both oxygen and H_2O_2. However, a linear dependence was found also in oxygen containing media, although with much higher currents, but with the same slope (even at different oxygen concentrations). This fact may trigger the development of such hybrid electrodes towards hydrogen peroxide sensors in different aqueous (including natural) samples.

1. Introduction

Organic/inorganic hybrid materials based on conjugated polymers and metallic oxides are getting growing interest due to their potential applications in various fields, as corrosion protection, electrocatalysis, or batteries [1,2]. Combination of magnetic iron-oxides with different conducting polymers is in the focus of research, since the high conductivity and high magnetic susceptibility of these composites can be exploited in different applications, such as electrical and magnetic shielding, nonlinear optics, magnetic electrocatalysis and as microwave absorbers [3]. During the last 10 years polypyrrole [4,5], polyaniline [6–8] and different polythiophenes [9–11] have been successfully combined with Fe_3O_4, γ-Fe_2O_3, α-Fe_2O_3 through various chemical procedures. Depending on the synthetic route, the resulted product can be either a bulk material or a micro/nano-particle hybrid. At the same time, deposition of thin conducting polymer layers on electrode surfaces can act as modified electrodes with advanced properties. The immobilization of iron-oxide nanoparticles into the polymeric film may also lead to additional catalytic behaviour. It is important to point out, that for electrocatalytic purposes electrodeposition is the best way to prepare these composites films, obtaining them directly on the electrode surface.

Due to their numerous favourable properties, application of conducting polymer (CP) based modified electrodes as electrocatalysts and sensors is in the focus of both scientific and industrial interest [12–14]. Their easy preparation, processability, low price, and relatively long lifetime all promote further studies in this field. Amperometric sensors, based on conjugated polymers such as polypyrrole, polyaniline and different polythiophene derivatives, have been successfully constructed for the determination and quantitative analysis of various compounds, such as ascorbic acid [15,16], dopamine [17], epinephrine [18] etc. More importantly, different studies proved that conjugated polymers can be used not only to catalyse the oxygen reduction reaction [19–21], but since the cathodic extra currents are proportional with the concentration of dissolved oxygen, this activity can be exploited in sensors, operating in the ppm range [22].

Electrochemical detection and sensing of H_2O_2 is still in the focus of R+D. The majority of such measurements is based on enzymatic biosensors [23], where specific interactions between an immobilized biomolecule (generally different enzymes) and hydrogen peroxide allows the sensitive measurement of the analyte. On the other hand, many efforts are devoted to the construction of non-enzymatic sensors for hydrogen peroxide [24,25], mainly motivated by their simplicity. Recently effective sensors have been developed, which have been based on transition metal

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hexacyanoferrates [26,27], and – in spite of their complex synthesis procedure – either their stability or their cost-effectiveness are attractive. However, in all systems the presence of oxygen is undesirable, since the potential windows of electrochemical oxygen- and H_2O_2-reduction overlap at almost all the applied electrodes; moreover, H_2O_2 is an intermediate of the oxygen reduction reaction [28,29], which makes the picture even more complicated. Due to this difficulty, such electrodes usually operate either under inert atmosphere (N_2, Ar) to exclude oxygen, or by sophisticated electrochemical methods (or using expensive electrode materials) to distinguish between the two species. Due to the above mentioned reasons, further studies towards cheap and easily synthesizable new modified electrodes are required.

In the field of H_2O_2 detection the most frequent application of conducting polymers is their utilization as immobilizing matrix of different enzymes [30–33], such as horseradish peroxidase (HRSP) or myoglobin, metal (especially Pt) nanoparticles [34], or mediators [35]. As for the direct detection of hydrogen peroxide, there are only a few recent trials in the literature: a special approach – using overoxidized polypyrrole – demonstrated by Debiemme–Chouvy recently [36], and one study based on PEDOT – and its combination with an organic dye, presented by C. Brett and his colleagues [37]. By incorporating inorganic nanoparticles or complexes into the matrix of the conducting polymer, sensors with significantly larger selectivity, sensitivity, and lifetime can be obtained. Such hybrids may allow parallel detection of different analyte (cysteine, ascorbic acid, dopamine, oxygen, hydrogen peroxide etc.). In order to achieve these goals various metals among other Au [38–40], Pt [41] and Cu [42] metal-oxides [43], metal-complexes [44,45] and their combination [46] have been successfully immobilized in different organic polymers. Among the metal oxides, magnetite (Fe_3O_4) is a promising candidate for electrocatalytic applications due to the Fe^{3+}/Fe^{2+} redox switching. This behaviour has been utilized in various processes, such as the O_2 or H_2O_2 reduction, both in the form of nanolayers, and immobilized nanoparticles [47–52].

Based on an easy synthesis procedure, presented by Deslouis et al., polypyrrole/magnetite hybrid thin layers have been synthesized in our research group recently [53]. We described the mechanism of the hybrid formation and proved its electrocatalytic activity in the ORR [54]. Moreover, we demonstrated that the enhanced catalytic activity of the hybrid is related to the electroreduction of the intermediate H_2O_2 on the incorporated magnetite nanoparticles. Although the catalytic effect of iron ions e.g. in the Fenton reaction is well-known, we can obtain a modified electrode through the immobilization of this mixed valence iron-oxide on the electrode surface.

For the above mentioned reasons, we decided to study the quantitative aspects of the electrocatalytic reduction of H_2O_2 on the polypyrrole/magnetite hybrid modified electrodes. In this work our aim is twofold: (i) to study the concentration dependence of the reduction of hydrogen peroxide on the PPy/Fe_3O_4 hybrid (ii) to investigate the effect of oxygen on the electrocatalytic behaviour of the hybrid, with respect to the possible determination of hydrogen peroxide in the presence of di-oxygen (e.g. in natural waters). Based on the results shown in the manuscript, we hope that such combination of cheap organic and inorganic materials may open new opportunities towards the easy detection of H_2O_2.

2. Experimental

2.1. Materials

Magnetite (Fe_3O_4) nanoparticles were synthesized by alkaline hydrolysis of iron(II) and iron(III) salts ($FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$, Sigma–Aldrich). The synthesis resulted magnetite nanoparticles with an average size around 12 nm. The characterization of the particles prepared in this way was reported elsewhere [55].

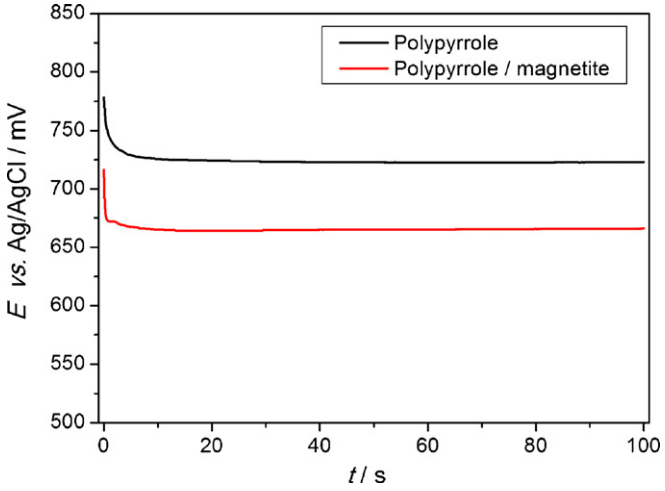

Fig. 1. Chrono-potentiometric curves registered during the galvanostatic synthesis ($3\,mA\,cm^{-2}$, $300\,mC\,cm^{-2}$) of Polypyrrole and the Polypyrrole/magnetite hybrid on Pt electrode.

Analytical grade pyrrole (Py) monomer and potassium tetraoxalate dihydrate (PTO) were purchased from Sigma–Aldrich. Pyrrole was freshly distilled before use. All polymerization solutions contained 0.1 M of the monomer pyrrole, and 0.05 M PTO in deionized water. The amount of magnetite particles was $10\,g\,dm^{-3}$. Polypyrrole (PPy) and polypyrrole-magnetite (PPy/Fe_3O_4) composite thin films were deposited galvanostatically at a current density of $j = 3\,mA\,cm^{-2}$ onto the working electrode with a charge density of $300\,mC\,cm^{-2}$. For further voltammetric studies the solution was changed after the polymerization to a 0.5 M phosphate buffer (pH = 7) in water.

2.2. Methods

The electrochemical measurements were performed on a PGSTAT 10 (Autolab) instrument in a closed, classical three electrode electrochemical cell. The working electrode was a platinum electrode with a size of $A = 1.00\,cm^2$. Ag/AgCl/3 mol dm^{-3} NaCl reference electrode, having a potential 0.200 V vs. SHE was used. All the potential values in the paper are given with respect of the silver/silver chloride electrode. Cyclic voltammograms of the thin films were registered at five different sweep rates (5, 10, 25, 50 and $100\,mV\,s^{-1}$). For the measurements in N_2 atmosphere, nitrogen gas was bubbled into the solutions for 30 min. Similar approach was followed for the experiments under O_2 atmosphere. The oxygen content was monitored by an Orion 3 Star oxygen sensor.

3. Results and discussion

3.1. Synthesis of polypyrrole and polypyrrole/magnetite layers

The polymerization procedure and the mechanism of the particle incorporation were described by our group very recently [54]. Both the neat polypyrrole and the polypyrrole/magnetite hybrid were synthesized galvanostatically with $3\,mA\,cm^{-2}$ current density under identical conditions, as described earlier. The chrono-potentiometric curves are presented in Fig. 1 for the deposition of both films on Pt electrode. The figure demonstrates that the shape of the curves is very similar to those reported previously. It is also clearly visible that – except a short transient period at the beginning – the potential value is almost constant during the whole deposition, which is related to the constant growth of the polymeric layer.