Oxidation of hydrogen at platinum-polypyrrole electrodes

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OXIDATION OF HYDROGEN AT PLATINUM-POLYPYRROLE ELECTRODES

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Abstract—Polypyrrole, an electronic conducting polymer, is used as a matrix for the dispersion of Pt particles. These particles can be included by two methods, *viz.* (1) by electrochemical deposition of platinum particles on a polypyrrole covered glassy carbon disc and (2) by incorporation of Pt particles during the polymerization of pyrrole on a glassy carbon disc. As a model reaction the oxidation of hydrogen at these electrodes is studied. The polypyrrole electrodes prepared by method (1) exhibit a good catalytic behaviour. The other type of electrodes however show, despite the higher Pt loading, much less activity. Additionally, electrodes were prepared according to method (1) with poly(*N*-methylpyrrole) and polyaniline as the conducting polymer. These electrodes show a similar diffusion limited behaviour for the oxidation of hydrogen as polypyrrole-modified electrodes, however the oxidation starts at a much higher potential.

INTRODUCTION

Recently, many researchers have studied the incorporation of catalyst particles in a polymer-modified electrode[1–6]. Two different methods have been applied. One method consists of the electrochemical metal deposition in a polymer film on a substrate, with the pores of the film filled with a solution, containing the appropriate metal salt. As well, insulating polymers[2, 3] and conducting polymers have been used[4, 5]. The other method consists of the incorporation of catalyst particles during formation of the polymer film[6].

For Pt particles deposited in a polymer film, mostly the evolution of hydrogen has been studied[3, 5]. It has been found that a polypyrrole film peeled off the substrate, due to hydrogen bubble formation at the polymer/substrate interface. To avoid the destruction of the platinum-polypyrrole electrode the oxidation of hydrogen has been chosen to characterize the electrocatalytic behaviour of platinum-polypyrrole electrodes. Glassy carbon (GC) has been used as electrode substrate to minimize background currents due to the oxidation of hydrogen at the substrate. Moreover, we have found that the adhesion of the polypyrrole film on a glassy carbon substrate is stronger than on metal substrates. Two different types of platinum-polypyrrole electrodes have been used. One type, denoted by Pt/PP/GC electrode, was prepared by the electrodeposition of platinum from PtCl_6^{2-} in a polypyrrole film on a glassy carbon disc and the other, denoted by Pt-PP/GC electrode, was prepared by precipitation of Pt particles with a diameter less than 44 μm , during the polymerization of pyrrole on a glassy carbon disc. The Pt particles were suspended in the solution, used for the polymer formation.

EXPERIMENTAL

A glassy carbon disc of 0.25 cm^2 served as the electrode substrate. Before polypyrrole deposition the

glassy carbon disc was polished with 0.3 μm alumina and cleaned in an ultrasonic bath. The polypyrrole films were formed on the glassy carbon from an aqueous solution of 0.1 M LiClO_4 and 0.14 M pyrrole at a constant potential, *viz.* 600 mV *vs* a saturated calomel electrode, or at a constant anodic current density ($i = 0.4 \text{ mA cm}^{-2}$). The thickness of the film was controlled by measuring the charge, q_F , used during the formation of the film. Unless otherwise stated, q_F was 100 mC cm^{-2} , corresponding to a film thickness of about 0.3 μm [7]. After the formation of the polypyrrole film, the electrode was thoroughly rinsed with distilled water.

The Pt/PP/GC disc electrodes were prepared by electrodeposition of Pt on and in a polypyrrole film, from an aqueous 0.07 M H_2PtCl_6 solution, at room temperature. The cathodic current density was constant during deposition. Assuming a 100% current efficiency for Pt^{4+} reduction, a charge of 100 mC cm^{-2} corresponds to a Pt loading of 51 $\mu\text{g cm}^{-2}$ or $2.6 \times 10^{-7} \text{ mol cm}^{-2}$. For the Pt-PP/GC electrodes we used Pt particles in the form of fine powdered metal dust; the particles were suspended in the polypyrrole formation solution. The diameter of these particles was less than 44 μm . By precipitation of platinum particles during polymerization of pyrrole on the glassy carbon disc, Pt particles were incorporated in the polymer layer. The amount of Pt incorporated in the film varied between 16 and 36 mg cm^{-2} , and was, moreover, very difficult to control.

All H_2 oxidation experiments were performed at 298 K in a thermostatted three-compartment cell, containing an aqueous solution of 0.5 M H_2SO_4 as supporting electrolyte. The solution in the working electrode compartment was saturated with H_2 . A reversible hydrogen electrode (*rhe*) was used as the reference electrode. The working electrode was rotated with speeds from 4 to 64 rotations per second. All *i*-*E* curves were recorded for an anodic potential sweep from 0 to 800 mV *vs rhe*, with a scan rate of 10 mV s^{-1} , in order to obtain reproducible results.

(A)

(B)

Fig. 1. SEM photographs of electrodes with electrochemically deposited Pt (A), magnification $9500\times$, and with incorporated Pt particles (B), magnification $450\times$.

Fig. 2. i - E curves for a bare Pt disc electrode (0.5 cm^2 geometric surface area) in $0.5 \text{ M H}_2\text{SO}_4$, saturated with H_2 , scan rate 10 mV s^{-1} .

RESULTS AND DISCUSSION

Electron micrographs

Figure 1 shows the scanning electron microscope pictures of the two types of electrodes. Their physical appearances are very different. At the Pt/PP/GC electrodes, the Pt particles are spherical and are regularly distributed over the polypyrrole surface. The particle size varies from 50 to 150 nm. At the

Pt-PP/GC electrodes the Pt particles have very irregular structures. The particle size varies from 4 to $44 \mu\text{m}$, and is 10–100 times larger than the thickness of the polypyrrole film. Consequently, the Pt-PP/GC electrodes have a very rough surface.

Surface area of platinum particles

To determine the true Pt surface area cyclic voltammograms of both types of electrodes in a solution of $0.5 \text{ M H}_2\text{SO}_4$, saturated with nitrogen, have been made in the potential range 0–1 V. The hydrogen adsorption and desorption peaks were ill-defined (see also Kao and Kuwana[3]).

Exclusively, one desorption peak was observed for electrodes with a high Pt loading (*viz.* $300 \mu\text{g cm}^{-2}$ and higher) and at high voltage scan rates (500 mV s^{-1} and higher). The determination of the charge needed for desorption of hydrogen on platinum was seriously hindered by the occurrence of the charge and the discharge curves for polypyrrole. When a potential range of 0–1.4 V was applied, a peak for reduction of a Pt-O compound was observed; its maximum occurred at 0.8 V. Application of a high potential, *viz.* 1.4 V, causes an irreversible oxidation of polypyrrole and a decrease in its conductivity, so that a correct determination of the Pt surface area is impossible. Both types of electrodes showed an almost identical behaviour. From these experiments it followed that it was not possible to determine the true surface area of the Pt particles in both types of electrodes.

Pt and PP/GC electrodes

To determine the catalytic behaviour of platinum-polypyrrole electrodes, first the oxidation of hydrogen at both bare Pt and polypyrrole electrodes was investigated. For a bare Pt electrode of 0.5 cm^2 , the current density is given in Fig. 2 as a function of electrode potential at various frequencies of rotation.

Fig. 3. Cyclic voltammogram for a glassy carbon electrode covered with a polypyrrole layer of 100 mC cm^{-2} formation charge ($0.3 \mu\text{m}$ thickness). Scan rate 10 mV s^{-1} .

Fig. 4. i - E curves for a Pt/PP/GC electrode with a Pt loading of $46 \mu\text{g cm}^{-2}$. The dashed line indicates the result of a PP/GC electrode without platinum under the same conditions.

Limiting current densities are reached at potentials higher than 90 mV *vs rhe* for all rotation speeds. The obtained limiting current densities agree to those measured by Harrison *et al.*[8], and are at maximum 10% smaller than the values that can be calculated with the Levich equation[9].

$$i_L = 0.620nFD_{\text{H}_2}^{2/3} \nu^{-1/6} c^s (2\pi f)^{1/2}$$

with: $D_{\text{H}_2} = 3.83 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [10], $\nu = 1.075 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ [11], $c^s = 7.232 \times 10^{-1} \text{ mol m}^{-3}$ [12].

Figure 3 shows the i - E curve for a stationary PP/GC electrode. Rotation of this electrode gives the same result; moreover, the same result is obtained when hydrogen is replaced by nitrogen. Consequently, the i - E curve of Fig. 3 has to be related to the charge and discharge of the polypyrrole film and no detectable hydrogen oxidation takes place at the polypyrrole film or at the substrate of the PP/GC electrode.

Pt/PP/GC electrode

Characteristic i - E curves for a Pt/PP/GC electrode with a Pt loading of $46 \mu\text{g cm}^{-2}$ are shown in Fig. 4. Limiting current densities are reached at potentials higher than 100 mV *vs rhe*. Figure 5 shows the limiting current densities as a function of the square root of the frequency of rotation for various Pt loadings and for a bare Pt electrode (dashed line). In Fig. 6 the limiting current density is plotted against the Pt loading, m_{Pt} , for two frequencies of rotation, *viz.* 25 and 64 Hz. Platinum was deposited with a constant current density of 0.4 mA cm^{-2} . The results indicate that Pt/PP/GC electrodes with a Pt loading of $50 \mu\text{g cm}^{-2}$ and more give almost the same results as a bare Pt electrode (dashed lines), and that at low Pt loadings, *ie* less than $50 \mu\text{g cm}^{-2}$, the curves clearly deviate from the experimental curve for the bare Pt electrode. This deviation is similar to that found for the oxidation of ferrocene and hydroquinone on a Pt electrode covered with an inert polymer film[13, 14]. In the latter case the difference between the experimental and the Levich diffusion limited current density is caused by the slow diffusion of the electroactive species through the polymer film[13, 14]. It is likely that the diffusion of H_2 through part of the polypyrrole film of a Pt/PP/GC electrode determines the $i_L/f^{1/2}$ relation (Fig. 5). At high Pt loadings the hydrogen is already practically completely oxidized on the Pt particles present on the outer surface of the electrode. For a Pt/PP/GC

Fig. 5. Variation of the limiting current density with the square root of the frequency of rotation for Pt/PP/GC electrodes with various Pt loadings. Pt loading: (x) $253 \mu\text{g cm}^{-2}$; (o) $101 \mu\text{g cm}^{-2}$; (□) $10 \mu\text{g cm}^{-2}$; (●) $0.05 \mu\text{g cm}^{-2}$. Pt deposition current density: 0.4 mA cm^{-2} . The dashed line gives the results for a bare Pt electrode.

Fig. 6. Plot of the limiting current density vs the Pt loading for Pt/PP/GC, at two rotating frequencies. The dashed lines indicate results for a bare Pt deposition current density: 0.4 mA cm⁻².

electrode with a low Pt loading the amount of Pt particles on the outer surface is less and not enough to oxidize completely the amount of hydrogen transported to the electrode at high rotation rates. Consequently, the diffusion of hydrogen from the outer surface of the polypyrrole film to the Pt particles inside the film affects the rate of hydrogen oxidation.

Because of the applied preparation method the Pt particles of a Pt/PP/GC electrode are clean, *ie* not covered by polypyrrole, so that the Pt surface is exposed to the solution. This conclusion is supported by the small difference in overvoltage for H₂ oxidation at a bare Pt electrode (Fig. 2) and a Pt/PP/GC electrode (Fig. 4).

Electrodes with a constant Pt loading of 102 μg cm⁻² were prepared at various constant current densities, *viz* from 0.04 to 8 mA cm⁻². It is likely that at high depositing rates the Pt particles are more concentrated on the outer surface of the film than at low depositing rates. This assumption is confirmed by the result of the

experiments, showing that the limiting current density for the oxidation of hydrogen increases with the current density for Pt deposition, for all frequencies of rotation.

Pt-PP/GC electrodes

For a Pt-PP/GC electrode, characteristic *i-E* curves are shown in Fig. 7. The shape of the curves differs strongly from the curves recorded for Pt/PP/GC electrodes. Moreover, the limiting current density is much less than for the Pt/PP/GC electrode with even the smallest Pt loading.

Figure 8 shows the limiting current density as a function of the square root of the frequency of rotation for two Pt-PP/GC electrodes with different Pt loadings. These curves are similar to those for Pt/PP/GC electrodes with a Pt loading less than 50 μg cm⁻². The limiting current densities are, however, lower despite a higher Pt loading. Analogously, also for a Pt-PP/GC

Fig. 7. *i-E* curves for a Pt-PP/GC electrode with a Pt loading of 24 mg cm⁻², recorded with a scan rate of 10 mV s⁻¹. The dashed line represents the results for a PP/GC electrode without Pt under the same conditions.

Fig. 8. Limiting current density for hydrogen oxidation *vs* the square root of the frequency of rotation for Pt-PP/GC electrodes with various Pt loadings (solid lines) and a bare Pt electrode (dashed line). Pt loading: (x) 36 mg cm⁻², (o) 24 mg cm⁻².

electrode the diffusion of hydrogen through a polypyrrole layer affects strongly the rate of hydrogen oxidation. This can be explained as follows: during the formation of a Pt-PP/GC electrode a thin film of polypyrrole is formed on the very well-conducting Pt particles, which are already adhered to the glassy carbon disc. The Pt-PP/GC electrodes have thus practically no clean Pt surface available for oxidation of hydrogen. This conclusion is supported by the differences in overvoltage for hydrogen oxidation at a bare Pt electrode (Fig. 2) and a Pt-PP/GC electrode (Fig. 7). The experimental results show that the electrochemical deposition of platinum in a polypyrrole film leads to a much better electrocatalytic electrode for the oxidation of hydrogen than if the incorporated platinum particles are covered with a thin polypyrrole film (Pt-PP/GC electrode).

Pt/PMP/GC and Pt/PAN/GC electrodes

Additionally, poly-methylpyrrole (PMP) and polyaniline (PAN) were used as the conducting polymer for the Pt/polymer/GC electrodes. Both polymers were

similarly prepared as polypyrrole using a formation charge of 100 mC cm⁻². The formation solution for PMP/GC electrodes consisted of 0.10 M Et₄NBF₄ and 0.11 M *N*-methylpyrrole in water, and for PAN/GC electrodes of an aqueous solution of 2 M HCl and 0.10 M aniline. A Pt loading of 102 μg cm² was deposited on these polymer-modified electrodes with a current density of 0.4 mA cm⁻².

Characteristic *i*-*E* curves are shown in Fig. 9 for a Pt/PMP/GC electrode and in Fig. 10 for a Pt/PAN/GC electrode. Hydrogen is not oxidized on a Pt/PMP/GC electrode at potentials lower than about 300 mV (Fig. 10) and on a Pt/PAN/GC electrode at potentials lower than 350 mV (Fig. 11). On a Pt/PP/GC electrode, however, hydrogen is oxidized at potentials only a few mV higher than *rhe* (Fig. 4). These differences in electrocatalytic activity are caused by differences in electron conductivity at the polymers at various potentials [15, 16]. A polymer in the oxidized state has a much better electron conductivity than in the reduced state.

Fig. 9. *i*-*E* curves for a Pt/PMP/GC electrode with a Pt loading of 102 μg cm⁻². The dashed line indicates the result of a PMP/GC electrode under the same conditions.

Fig. 10. *i*-*E* curves for a Pt/PAN/GC electrode with a Pt loading of 102 μg cm⁻². The dashed line indicates the result of a PAN/GC electrode under the same conditions.

Hydrogen oxidation is a diffusion limited process for all the investigated Pt/polymer/GC electrodes at high potentials, viz. $E > 450$ mV vs *rhe*, as follows from the dependence of the current density on the frequency of rotation (Figs 4, 9 and 10).

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