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OHMIC RESISTANCE OF POLYPYRROLE-MODIFIED ELECTRODES WITH INCORPORATED Pt PARTICLES

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Abstract—The ohmic resistance of polypyrrole modified electrodes has been determined as a function of the potential by the ac impedance method. It has been found that polypyrrole-modified electrodes have a negligible ohmic resistance in the potential region from 0.2 to -0.2 V vs see. When the potential is decreased from -0.2 to -0.3 V, the ohmic resistance shows a sharp increase, due to the transition of polypyrrole from the oxidized, conducting state to the reduced, insulating state. The electrodeposition of Pt particles in the film does not change the resistance at high potentials, but does decrease the rise in ohmic resistance at low potentials. Moreover, this decrease depends on the current density, used for the deposition of the particles.

INTRODUCTION

Conducting polymers have grown in importance in electrochemical research. Recently, attention has been paid to the incorporation of catalyst particles in a polypyrrole matrix, especially of metal particles by reduction of the appropriate metal salt\[1-5\]. In particular, the use of Pt particles seems to be very profitable. The application of these metal-polymer electrodes for the oxidation of hydrogen has been a subject of our research\[6\]. In order to characterize these electrodes, the ohmic resistance was determined as a function of the potential of the electrode, with incorporation of various quantities of Pt. The effect of the current density, used for the electrodeposition of these particles, upon the resistance was investigated.

EXPERIMENTAL

The impedance measurements were carried out at 293 K in a one-compartment cell of about 200 cm\(^3\), containing an aqueous solution of 2 M HCl. Two large (50 cm\(^2\)) platinized Pt counter electrodes were used, symmetrically placed with respect to the working electrode (0.25 cm\(^2\)), facing upwards in order to avoid accumulation of evolved gas. A saturated calomel electrode (see) served as a reference electrode; all potentials are given with respect to this electrode. The impedance of the cell was measured using a Solartron 1250 Frequency Response Analyzer with an electrochemical interface, coupled with a HP microcomputer. A sinusoidal voltage, with an amplitude of 0.01 V and a frequency range from 128 to 65,000 Hz, was superimposed on the bias potential of the electrode, which was varied from 0.2 to -0.35 V, in steps of 0.05 V, with a time span of ca 5 min between the subsequent potential steps.

A Pt-disc electrode (0.25 cm\(^2\)) was used as the substrate for the polypyrrole films. Before the deposition of polypyrrole, the Pt electrode was pretreated by the following method. For 1 min, oxygen was vigorously evolved at the electrode, at a potential of 3.5 V vs see in an aqueous solution of 0.5 M H\(_2\)SO\(_4\), to remove impurities and polypyrrole deposits, used in the preceding experiment. The electrode was pulsed between -1.0 and 2.5 V, for 2 min. Finally, the potential of the electrode was cycled between 0 and 1.5 V, with a scan rate of 1 V s\(^{-1}\), until the cyclic voltammogram showed a clean Pt surface. Impedance measurements were carried out with this clean electrode as a blank.

Polypyrrole (PP) was formed on the clean Pt substrate by anodic oxidation of pyrrole from an aqueous solution of 0.14 M pyrrole and 0.1 M (C\(_2\)H\(_4\)NBF\(_4\), at a constant current density of 0.4 mA cm\(^{-2}\). The charge, passed during formation of the film was 100 mC cm\(^{-2}\), this corresponds to a film thickness of 0.28 \(\mu\)m, assuming a density of 1.48 g cm\(^{-3}\)[7]. The electrode (PP/Pt electrode) was used as the working electrode in impedance measurements.

After the impedance measurement with the polypyrrole electrode, Pt particles (for particle distribution, see[6]) were deposited at a constant current density, ranging from 0.08 to 8 mA cm\(^{-2}\), on and in the polypyrrole film, present on the Pt substrate, to prepare a platinum/polypyrrole electrode (Pt/PP/Pt electrode). A one-compartment cell, filled with a solution of 0.02 M H\(_3\)PtCl\(_6\) and 2 M HCl, was used. The Pt was deposited in steps, with a charge, \(Q_{\text{Pt}}\), of about 200 mC cm\(^{-2}\) per step, corresponding to 102 \(\mu\)g Pt cm\(^{-2}\). Between the subsequent steps, the impedance measurements were carried out.

RESULTS AND DISCUSSION

The ohmic resistance of the cell was determined from the complex plane plot, in which for various frequencies the imaginary component of impedance, \(Z'\), was plotted as the real component of the impedance, \(Z''\). The intersection of the \(Z'/Z''\) curve with the \(Z''\)-axis at \(\omega \rightarrow \infty\) denotes the ohmic resistance of the cell. Due to the
very large surface area of the counter electrodes and the construction of the cell, the resistance is caused by the resistance of the working electrode and by the resistance of a solution layer adjacent to the working electrode[8].

Pt electrodes

The $Z''/Z'$ curve for a Pt electrode showed the expected shape, viz. at potentials higher than $-0.3 \text{ V}$ a straight line, making an angle with the $Z'$-axis of almost 90°. At potentials below $-0.3 \text{ V}$ hydrogen bubbles, formed at the electrode surface, affect the $Z''/Z'$ curve, and an accurate determination of the ohmic resistance was not possible. For the bare Pt electrodes the ohmic resistance is constant in the potential region from $+0.2 \text{ to } -0.3 \text{ V}$ and is equal to $1.5 \pm 0.2 \text{ } \Omega$. This resistance is only determined by the resistance of the solution layer adjacent to the electrode, since the resistance of the Pt electrode is negligible.

PP/Pt electrode

Characteristic $Z''/Z'$ curves for PP/Pt electrodes are given in Fig. 1. At potentials higher than $-0.2 \text{ V}$ an intersection of the $Z''/Z'$ curve with the $Z'$-axis occurs. To obtain the ohmic resistance, $R$, at potentials lower than $-0.2 \text{ V}$ extrapolation to $\omega \to \infty$ is necessary.

Figure 2 shows for a PP/Pt electrode the ohmic resistance as a function of the potential. In the potential region from $+0.2 \text{ to } -0.2 \text{ V}$ the ohmic resistance is constant. The average value (averaged for about 10 PP/Pt electrodes) is $1.45 \pm 0.09 \text{ } \Omega$.

From Fig. 2 it follows that between $-0.2$ and $-0.35 \text{ V}$ the ohmic resistance increases sharply, and a hysteresis effect is clearly observed. Above $0.05 \text{ V}$ the hysteresis has practically disappeared.

The increase in ohmic resistance in the potential region from $-0.2 \text{ to } -0.35 \text{ V}$ is indicated by $\Delta R_0$ and is defined as the difference between the average ohmic resistance at $-0.30$ and $-0.35 \text{ V}$ and the ohmic resistance at $+0.2 \text{ V}$. For about 10 PP/Pt electrodes the average value of $\Delta R_0$ is $4.5 \pm 0.6 \text{ } \Omega$.

For a reduced polypyrrole electrode (surface area $0.5 \text{ cm}^2$), assuming a film thickness of $0.28 \mu\text{m}$, $\Delta R_0 = 4.5 \text{ } \Omega$ is equivalent to a conductivity of $1.24 \times 10^{-5} \text{ S cm}^{-1}$.

The ohmic resistance for a PP/Pt electrode consists of a part related to a solution layer, which does not depend on the potential, and a part related to the polypyrrole film. In the high potential region the ohmic resistance is, within error limits, the same for both Pt and PP/Pt electrodes. This leads to the conclusion that in the high potential region polypyrrole is very well conducting, which is in agreement with published results[7].

The slight decrease in ohmic resistance, occurring when a polypyrrole film is deposited on a Pt substrate (see Fig. 2), can be explained by an increase of surface roughness. By a potential decrease from $-0.2$ to $-0.3 \text{ V}$ the oxidized state of polypyrrole is converted to its reduced state. It is well known that the oxidized polypyrrole is a good electron-conductor and the reduced polypyrrole is a poor electron-conductor[7]. The transition from oxidized to reduced polypyrrole causes an increase of ohmic resistance of the polypyrrole film.
Additional experiments showed that the time, passed between the subsequent potential steps in the ac impedance experiments is larger than the response time of the film. So, there should be no apparent reason for the observed hysteresis effect. We must therefore conclude that the hysteresis may be caused by irreversible changes in structure of polypyrrole during the reduction of the film. These changes are not restored by a potential increase from $-0.2$ to $+0.2$ V. The effect of the irreversible reduction of the film is only measurable for the reduced film because of its low conductivity.

Pt/PP/Pt electrodes

For Pt/PP/Pt electrodes the shape of the $Z''/Z'$ curves was the same as for PP/Pt electrodes. Also the ohmic resistance in the high potential region ($E > -0.2$ V) is equal for both types of electrodes. Ohmic resistance vs potential curves for Pt/PP/Pt electrodes with various Pt loadings are shown in Fig. 3. From Fig. 3 it can be deduced that the rise of the ohmic resistance between $-0.2$ and $-0.35$ V, $\Delta R$, decreases with increasing Pt loading. Because both for PP/Pt electrodes and for the Pt/PP/Pt electrodes $\Delta R_0$ and $\Delta R$, respectively, showed a rather large spread, it is more useful to make use of the reduced increase of ohmic resistance, $\Delta R^*$ as defined by $\Delta R/\Delta R_0$.

In Fig. 4(a-c), for two series of experiments $\Delta R^*$ is plotted vs the charge, which was used for electrodeposition of Pt, at various current densities of deposition.

Figure 4 shows that $\Delta R^*$ decreases with increasing Pt loading and approaches a limiting value. $\Delta R^*$ is affected by the current density of Pt deposition. From

![Fig. 3. Ohmic resistance vs potential curves for a Pt/PP/Pt electrode with various Pt loadings: (a) 200, (b) 400, (c) 600, (d) 800 and (e) 1000 mCcm$^{-2}$.](image)

![Fig. 4. $\Delta R^*$ vs charge used for deposition of Pt particles with various current densities of Pt deposition. For each current density the results of two series of experiments are given. (a) $i_{Pt} = 0.08$ mA cm$^{-2}$; (b) $i_{Pt} = 0.8$ mA cm$^{-2}$; (c) $i_{Pt} = 8.0$ mA cm$^{-2}$.](image)
Fig. 4(a)–(c) it follows that Pt/PP/Pt electrodes with Pt particles, formed at a low current density (0.08 mA cm\(^{-2}\)) show the sharpest decline of $\Delta R^*$ at low Pt loading and the largest spreading in $\Delta R^*$. For electrodes prepared with a higher current density of Pt deposition, $\Delta R^*$ shows a more gradual decrease with increasing Pt loading. Especially, for electrodes prepared with $i_{\text{Pt}} = 8$ mA cm\(^{-2}\), the spreading in $\Delta R^*$ is very small.

As can be seen in Fig. 3, the incorporation of Pt particles has little effect on the ohmic resistance in the potential region where polypyrrole is in the oxidized, conducting state. When polypyrrole is reduced, the electrical conductance of the polymer film will be partly taken over by the Pt particles, incorporated in the film. This explains the decrease of $\Delta R^*$ with increasing Pt loading.

The differences in decrease of $\Delta R^*$ between Pt/PP/Pt electrodes, prepared with various current densities of Pt deposition, are caused by differences in distribution of the particles within the film. As pointed out in a previous paper[6], Pt particles, deposited with a low current density, are distributed throughout the polypyrrole film. The particles when more enhance the electrical conductivity of the whole Pt/PP film, even at low Pt loading. The conductance is then for a smaller part determined by the polypyrrole chains. The contact between the Pt particles is of greater importance to the ohmic resistance. When the particles are distributed over a large space, small fluctuations in the distribution have a large effect on $\Delta R^*$.

At the Pt/PP/Pt electrodes, prepared with a high current density for Pt deposition, the particles are first and mainly deposited on the outer surface and layer of the polypyrrole film (electrolyte-side). This is observed with a microscope. In this case a good electrical contact between the particles exist and different electrodes show a small spread in $\Delta R^*$.

**Ageing of PP/Pt electrodes**

The influence of the low electrode potential, which was used for deposition of Pt particles, on the ohmic resistance of PP/Pt electrodes was investigated. A PP/Pt electrode in 2 M HCl was held at a potential of +0.1 V vs sce at low potentials (-0.2 to -0.35 V). The reason for this decrease is not yet known.

**CONCLUSION**

From the determination of the ohmic resistance follows that polypyrrole has a high electrical conductivity in the potential region from -0.2 to +0.2 V vs sce.

Between -0.2 and -0.3 V a sharp rise of the resistance is observed, due to the transition of the oxidized polypyrrole to the reduced state.

Incorporation of Pt particles in the film causes a decrease of the increase of ohmic resistance, because the particles contribute partly to the electrical conductivity.

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