The reduction of dioxygen at polypyrrole-modified electrodes with incorporated Pt particles

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THE REDUCTION OF DIOXYGEN AT POLYPYRROLE-MODIFIED ELECTRODES WITH INCORPORATED Pt PARTICLES

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Abstract—The electrodeposition of Pt particles in a polypyrrole layer leads to electrodes, showing electrocatalytic activity for the reduction of dioxygen in aqueous media. The electrode preparation, with the current density and time of deposition as main parameters, influences the final product composition, i.e., the ratio of water to hydrogen peroxide, as dioxygen can be reduced to water or hydrogen peroxide, respectively, via a four- or a two-electron mechanism. By using the rotating ring-disc technique the amount of hydrogen peroxide in the reaction product can be detected. When Pt particles are deposited with a high current density, mainly water is produced. At low current densities of Pt deposition, hydrogen peroxide is the main product. These effects are explained in terms of the availability of the Pt surface for dioxygen.

1. INTRODUCTION

In a previous paper[1], we showed that the incorporation of Pt particles in a polypyrrole layer leads to an electrode system which shows electrocatalytic activity for the oxidation of hydrogen. When platinum is deposited electrochemically, the particles are distributed three-dimensionally in the layer, due to the porosity of the polymer[2]. We have studied the reduction of dioxygen in aqueous solution as a second model system, as this is a highly interesting and important reaction in eg fuel cell and battery technology. This reaction also offers the opportunity to study the influence of electrode preparation on the composition of the final product, as dioxygen can be reduced to water via a four-electron mechanism and/or to hydrogen peroxide via a two-electron mechanism.

Pyrrrole itself shows little activity for the reduction of dioxygen. Okabayashi[3] reported no catalytic activity at all for a polypyrrole-modified electrode, whereas Jakobs et al[4] have shown electrocatalytic activity of polypyrrole for the reduction of dioxygen. Jakobs et al showed, in a rotating ring-disc experiment, that the activity decreases and the selectivity for the four-electron reduction increases with increasing thickness of the polypyrrole layer on a Pt substrate. This has been ascribed to a high decomposition rate of hydrogen peroxide in the polymer film, favoured by slow diffusion rates of dioxygen and hydrogen peroxide in the film.

Electrocatalysts for the reduction of dioxygen can be incorporated in a polymer film on a substrate electrode in several ways. Anionic complexes can be incorporated as electrocatalytically active counter ions during the electrochemical synthesis of the polypyrrole layer. Examples are the incorporation of iron- and cobalt-tetrasulfonato phthalocyanines[3, 5–7] The use of "simple" cobalt complexes like cobalt acetate, benzoyl or acetylacetone has been reported, although the active species in the polymer have not been identified[8]. The electrodes with Co- or Fe-phthalocyanine doped polypyrrole layers show in acid media, respectively a two- and/or a four-electron reduction process to hydrogen peroxide and water.

The incorporation of particles during the polymerisation of polypyrrole is also possible. Noufi[9] reported that RuO₂⁺ ions to RuO₂ particles after synthesis of the polymer layer. These RuO₂ particles were then active for the evolution of dioxygen. The inclusion of large Pt particles during the polymerisation of pyrrrole leads to electrodes with a low activity. Coor Fe-phthalocyanine, has led to electrode systems, which were electrocatalytically active for the reduction of dioxygen[10].

2. EXPERIMENTAL

A rotating ring-disc electrode (rrde) system has been used for measuring the activity and selectivity of the reduction process[11]. The rrde assembly consisted of a pyrolytic graphite (Cp) disc of 0 524 cm², surrounded by an insulating gap and a Pt ring at 0 145 cm². The characteristic radii of the electrode, R₁, R₂ and R₃ (see Fig 1) were 4 08, 4 41 and 4 91 mm respectively. The collection efficiency, N, of the electrode was 0 24 (both calculated from the geometry of the electrode and measured from the reduction of dioxygen to hydrogen peroxide at Co-phthalocyanine).

Before each deposition of polypyrrole, the electrode was polished with 0 3 and 0 05 µm alumina to a mirror-like finish, followed by cleaning in an ultrasonic bath for ca 1 min and rinsing with distilled water. The ring electrode was pulsed between vigorous O₂ and H₂ evolution (at +20 and -20 mA) and...
platinized with a current of $-2 \text{ mA}$ during 30 s and $-1 \text{ mA}$ during 60 s, in order to obtain high activity for $\text{H}_2\text{O}_2$ oxidation.

The polypyrrole layer was formed on the disc electrode, by electrochemical oxidation of the monomer pyrrole, from an aqueous solution of 0.1 M pyrrole and 0.1 M tetraethylammonium perchlorate or tetrafluoroborate, in a one-compartment cell with a Pt foil counter electrode. A constant current density of $0.4 \text{ mA cm}^{-2}$ was used, until a total charge of $100 \text{ mC cm}^{-2}$ was passed, corresponding to a thickness of ca $0.28 \mu \text{m}$.

Platinum was deposited in and on to the polypyrrole layer from an aqueous solution of 2 M HCl and 0.07 M H$_2$PtCl$_6$, by electrochemical reduction of the Pt$^{4+}$-ions. A constant current density was applied during deposition, the amount of Pt was controlled by measuring the charge, passed during deposition. Assuming a 100% current efficiency for Pt$^{4+}$-reduction, a charge $Q_{pt}$ of $100 \text{ mC cm}^{-2}$ corresponds to a Pt loading of $51 \mu \text{g cm}^{-2}$ or $2.6 \times 10^{-10} \text{ mol cm}^{-2}$. The current densities used were 0.08, 0.80 and $8 \text{ mA cm}^{-2}$.

Finally, the ring electrode was again pulsed between 0.7 and $H_2$ evolution, in order to remove adsorbed pyrrole species.

The oxygen-reduction experiments were carried out in a 150 ml three-compartment cell. As counter electrode served a Pt foil, separated from the working-electrode compartment by a porous glass filter. A reversible hydrogen electrode was used as the reference electrode. All potentials will be given with respect to this electrode. The reference-electrode compartment was connected with the working-electrode compartment by a Luggin capillary.

The cell was filled with an aqueous 0.5 M H$_2$SO$_4$ solution, saturated with O$_2$ at a pressure of 100 kPa. The oxygen-reduction experiments were carried out at a temperature of 293 K. The electrode assembly was rotated with a speed of 25 Hz (rps).

The measurements were carried out by imposing a triangular potential sweep upon the disc electrode, while the potential of the ring electrode was kept at a constant potential of 1.20 V vs. rHE, the potential where $H_2O_2$ is oxidized. The potential of the disc was cycled between 0.8 and 0.0 V vs. rHE with a scan rate of $50 \text{ mV s}^{-1}$.

A Tacussel Bi-Pad potentiostat and a Wenking VSG 72 scan generator were used to control the potentials of the electrodes, and the ring and disc currents were recorded as a function of the disc potential, using a Hewlett Packard 7046 dual pen x-y recorder.

The disc currents were corrected by subtracting the disc currents in $N_2$-saturated solution, because of the large "background" currents, due to the charged, porous polypyrrole layer. The ring current at $E_{ring} = +0.8 \text{ V vs rHE}$ was subtracted from the measured ring currents, to compensate for $H_2O_2$, present in solution from previous experiments.

### 3. THEORY

The reduction of dioxygen in acid solution can proceed according to [12]

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}, \]  
\[ \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2, \]

The hydrogen peroxide, formed by (2), can be further reduced, according to (3), or chemically decomposed, according to (4)

\[ \text{H}_2\text{O}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O}, \]
\[ 2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O}. \]

As the last two reactions give the products water and/or dioxygen, effectively the reduction of dioxygen leads to the formation of water and/or hydrogen peroxide as the final products. Therefore, the disc current can be thought of as consisting of two components (a) the current due to the reduction of dioxygen molecules which give water as the final product and (b) the current caused by the reduction at dioxygen molecules which lead to hydrogen peroxide as the final product

\[ I_D = I_D(H_2O) + I_D(H_2O_2). \]

Also, we define the reduction rate of dioxygen molecules in moles per second as $n_O_2$ and the number of dioxygen molecules which give $H_2O$ and $H_2O_2$, respectively as $n_{H2O}$ and $n_{H2O2}$, so $n_{H2O} = n_{H2O} + n_{H2O2}$. These values are divided by the amount of Pt present on the disc electrode to give the "reduced" reaction rates $n_{H2O}^*$, $n_{H2O2}^*$ and $n_{H2O_2}^*$ for the total reaction, the reduction to $H_2O$ and the reduction to $H_2O_2$, respectively. The fraction of the reduced dioxygen molecules which lead to $H_2O$ as the final product is called $x_{H2O}$, and thus $x_{H2O} = n_{H2O}/n_{O_2}$.

It follows that

\[ I_D(H_2O) = -4x_{H2O} n_{O_2} F, \]
\[ I_D(H_2O_2) = -2(1 - x_{H2O}) n_{O_2} F \]

So

\[ I_D = -2(1 + x_{H2O}) n_{O_2} F \]

The ring current gives the amount of hydrogen peroxide, formed at the disc

\[ -I_R = I_D(H_2O_2) N, \]
Reduction of dioxygen at polypyrrole-modified electrodes

The cyclic voltammogram for a Pt/PP/Cp electrode is given in Fig 2. This figure shows that the reduction of dioxygen starts at a more anodic potential than when an electrode without Pt particles is used. The cathodic scan (to the part of the potential sweep from +0.8 V to 0.0 V) gives a limiting disc current at ca 0.1 V. We have taken the currents from the cathodic sweep at this potential, at a rotation speed of 25 Hz, to calculate the half-wave potential $E_{1/2}$ and the "turnover-numbers", as described in the preceding paragraph.

4 RESULTS

The half-wave potentials for Pt/PP/Cp electrodes prepared with various current densities (c.d's) of Pt deposition are shown in Table 1. This table shows that $E_{1/2}$ increases with increasing Pt loading, the effect being more pronounced at a low deposition rate. The change in $E_{1/2}$ is directly associated with the efficiency for H$_2$O production, shown in Fig 3. When using a deposition current of 0.8 mA cm$^{-2}$, all the dioxygen will be reduced to give H$_2$O as the final product, except at the lowest Pt loading. The experiments with lower Pt deposition c.d's show a sharp increase of $x_{H_2O}$ from $Q_{Pt}=150$ mC cm$^{-2}$ onwards, corresponding to higher $E_{1/2}$ values.

In Figs 4-6 the values of, respectively, $n_{O_2}$, $n_{H_2O}$, and $n_{H_2O_2}$ are shown as a function of the Pt loading for various Pt deposition c.d's. The plots of $n_{O_2}$ and $n_{H_2O}$ show the same behaviour as $x_{H_2O}$ in Fig 3, and a sharper increase with increasing Pt loading for $I_{Pt}=0.8$ mA cm$^{-2}$, compared to the curve for $I_{Pt}=0.08$ mA cm$^{-2}$. The highest c.d for Pt deposition shows a high constant $n_{O_2}$, while $n_{H_2O}$ decreases. However, when the values are corrected for the total amount of Pt present (leading to $n_{O_2}$ and $n_{H_2O}$) the efficiencies change drastically. At low Pt deposition rate only a small increase of $n_{O_2}$ and $n_{H_2O}$ remains, and for the highest rate of Pt deposition $n_{O_2}$ and $n_{H_2O}$ decrease with increasing Pt loading.
Fig 4 \( \frac{n_{\text{O}_2}}{10^9 \text{mol s}^{-1}} \) and reduced reaction rate for \( \text{O}_2 \) reduction \( (\text{n}^*_{\text{O}_2}) \) vs the Pt loading for \( \text{i}_{\text{p}} = (A) 0.08, (B) 0.80, (C) 8.0 \text{ mA cm}^{-2} \)

\[ \text{Fig 5 Rate of reduction to } \text{H}_2\text{O} (\text{n}_{\text{H}_2\text{O}}) \text{ and reduced reaction rate for } \text{H}_2\text{O} \text{ production } (\text{n}^*_{\text{H}_2\text{O}}) \text{ vs the Pt loading for } \text{i}_{\text{p}} = (A) 0.08, (B) 0.80, (C) 8.0 \text{ mA cm}^{-2} \]

\[ \text{Fig 6 Rate of reduction to } \text{H}_2\text{O}_2 (\text{n}_{\text{H}_2\text{O}_2}) \text{ and reduced reaction rate for } \text{H}_2\text{O}_2 \text{ production } (\text{n}^*_{\text{H}_2\text{O}_2}) \text{ vs the Pt loading for } \text{i}_{\text{p}} = (A) 0.08, (B) 0.80, (C) 8.0 \text{ mA cm}^{-2} \]

For the experiments with the lowest Pt deposition c.d. \( n_{\text{H}_2\text{O}_2} \) remains almost constant \( (n^*_{{\text{H}_2\text{O}_2}}) \) shows therefore a steady decrease), for \( \text{i}_{\text{p}} = 0.8 \text{ mA cm}^{-2} \), a sharp decrease of \( n_{\text{H}_2\text{O}_2} \) can be seen at the highest Pt loading The experiments with the highest Pt deposition rate show no formation of hydrogen peroxide

5. DISCUSSION

5.1 High Pt deposition current

For the experiments, using the highest c.d. of Pt deposition, the situation is quite clear As has been found for the oxidation of hydrogen[1], in this case
the Pt particles are deposited mainly on the surface (polymer/electrolyte interface) of the polypyrrole layer. The electrodes show a behaviour similar to that of a bare Pt electrode, i.e. dioxygen is completely reduced to water. From the plots of $n^0$ and $n^0_{\text {rec}}$ vs Pt loading, it can be seen that the deposition of a small amount of Pt ($1.3 \times 10^{-7}\text{ mol cm}^{-2}$ or $25.6 \mu\text{g cm}^{-2}$) is sufficient to reduce most of the dioxygen to $\text{H}_2\text{O}$.

5.2 Low Pt deposition current

For the lowest Pt deposition c d's, the situation is more complicated. A higher amount of $\text{H}_2\text{O}_2$ is formed at these electrodes. In reference[1] it has been concluded that the Pt particles in this case are dispersed over the entire polymer layer. At low Pt loading this leads to a low reduction rate of dioxygen, caused by a slow diffusion of dioxygen molecules into the polymer layer. The high amount of peroxide formed is caused by the fact that only a small part of the deposited platinum is available for dioxygen, this leads to a shift in product composition towards hydrogen peroxide[12, 13].

This conclusion is supported by the work of Elzing[6], who showed that the shift of the half-wave potential in the anodic direction is caused by the increase of the number of active sites. An increase of the number of sites by a factor $p$ then produces a shift of the half-wave potential of

$$AF_{1/2} = \frac{RT}{aeF} \ln p,$$  \hspace{1cm} (12)

in which $n$ is the number of electrons, involved in the rate determining reaction. Generally, the shift of the half-wave potential for a ten-fold increase of the number of active sites is equal to the Tafel slope. As the dominating reaction (the formation of water or the production of hydrogen peroxide) changes when the Pt loading is increased, the Tafel slope is not the same for all electrodes and the "exact" increase in active sites cannot be determined. However, qualitatively it is concluded that the number of active sites increases sharply with increasing Pt loading.

As the Pt loading increases, more Pt will be deposited near the polymer/electrolyte interface. This shortens the diffusion path and thus increases $n_{\text{rec}}$. More Pt will be available for reduction, which leads to an increasing amount of water as the final product.

6. CONCLUSIONS

The reduction of dioxygen at Pt/PP/Cp electrodes depends on how the Pt particles are incorporated in the polymer. The deposition of Pt with a high c d leads to electrodes with most of the particles situated near the surface of the polypyrrole layer (i.e. near the polymer/electrolyte interface). This leads to a high conversion rate of dioxygen and, because a large area of Pt is then available for reduction, to a high selectivity for the formation of $\text{H}_2\text{O}$ ($\text{H}_2\text{O}_2 < 1$).

When particles are deposited at lower rates, they are more evenly distributed over the whole film, leading to a low conversion rate of dioxygen. This also leads to a lower availability of Pt for reduction, causing the main product to be hydrogen peroxide. Increasing the Pt loading then gives rise to a higher reduction rate of dioxygen and a shift in product composition from hydrogen peroxide towards water. The last effect offers a unique method for changing the electrode properties.

During the experiments, polypyrrole served as an excellent conducting matrix for the dispersion of the Pt particles. The three-dimensional conducting layer gives the opportunity to change the distribution of electrodeposited catalyst particles, by varying the deposition rate. However, it must be remarked that the experiments described here, were carried out on a small time scale. It is known that polypyrrole is sensitive to hydrogen peroxide[4], as well as to other oxidizing agents, which destroy the conducting "back-bone" of the polymer. In a cycling experiment, carried out in an $\text{O}_2$-saturated solution, the disc currents steadily decrease. This is caused by the instability of the polymer itself and by the attack of hydrogen peroxide on the conducting polymer support, as the reduction of oxygen leads to an accumulated amount of hydrogen peroxide in solution.

REFERENCES