Application and characterization of polypyrrole-modified electrodes with incorporated Pt particles

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APPLICATION AND CHARACTERIZATION OF POLYPYRROLE-MODIFIED ELECTRODES WITH
INCORPORATED Pt PARTICLES

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ABSTRACT

Polypyrrole films of 0.3 μm thickness have been deposited on a carbon (vitreous carbon or pyrolytic graphite) or platinum substrate. Platinum particles have been deposited on this polymer layer in two ways. Firstly, by electrodeposition of the particles in and on the polymer layer by reduction of Pt^{4+} ions after the formation of polypyrrole, and secondly, by simultaneous deposition of polypyrrole and precipitation of Pt powder particles. Electrodes, prepared by the former method, proved to be electrocatalytically active for the oxidation of hydrogen in aqueous 0.5 M H_2SO_4 , with high current densities at low Pt loading and low overpotential. The latter method produced electrodes with Pt particles, mostly inactive for the oxidation of H_2 . The electrodes with electrodeposited Pt particles were also active for the reduction of dioxygen, yielding (relatively) more H_2O with increasing Pt loading and increasing rate of Pt deposition.

A characterization of the electrodes with incorporated Pt particles was carried out, using AC-impedance techniques. The ohmic resistance of the electrodes was determined as a function of the electrode potential and the Pt loading. The ohmic resistance of the electrodes increased, going from -0.2 V to -0.3 V vs SCE, due to the (partial) reduction of the polymer. Loading the polymer layer with Pt particles decreased the resistance at low potential (< -0.2 V vs SCE), depending on the rate of Pt deposition.

INTRODUCTION

It has been reported that metal particles can be deposited on a conducting polymer layer, by reduction of the corresponding ions [1-4]. Because of the porosity of polypyrrole and polythiophene layers, the particles will be deposited

not only on the outer surface of films of these polymers, but also close to the polymer-substrate interface [1,4]. We have studied the electrocatalytic possibilities of electrodes with Pt particles, incorporated in a polymer layer, regarding the oxidation of hydrogen and the reduction of dioxygen.

EXPERIMENTAL

The polypyrrole layers were deposited on a glassy carbon, pyrolytic graphite, or platinum disc electrode of 0.25 cm^2 from an aqueous solution of 0.1 M pyrrole and 0.1 M tetraethylammonium tetrafluoroborate, with a current density of 0.4 mA.cm^{-2} . The layers were ca. $0.3 \text{ }\mu\text{m}$ thick (100 mC.cm^{-2} charge passed during deposition).

Pt particles were incorporated in the polymer layer by : (1) reduction of Pt^{4+} from an aqueous solution of 2 M HCl and $0.07 \text{ M H}_2\text{PtCl}_6$ with constant current density after formation of the polymer (particle size: 50-150 nm) and (2) by precipitation of Pt powder particles during the formation of the polymer (particle size: $<40 \text{ }\mu\text{m}$).

AC impedance measurements were carried out to determine the ohmic resistance of electrodes, in a one-compartment cell, filled with 2 M HCl. The real part of the complex impedance at high measuring frequency then consists of the ohmic resistance of the working electrode and of a small solution layer adjacent to the electrode [5,6].

RESULTS

Ohmic resistance [7]

The ohmic resistance of a polypyrrole electrode as a function of the electrode potential is shown in Fig. 1. The resistance increases at potentials lower than -0.2 V vs SCE , due to the partial reduction of the polymer. The incorporation of Pt particles, by electrodeposition, causes a decrease of the ohmic resistance at low potentials, due to the contribution of the particles to the conductivity; this is shown in Fig. 2.

The relative decrease of the ohmic resistance when Pt particles are incorporated in the polymer depends on the rate of deposition, as shown in Fig. 3 for two series of experiments. The lowest deposition rate shows the most sharp decrease with increasing Pt loading and a large spread in the results, this indicates that the particles are deposited more near the polymer-substrate interface. Increasing the rate of deposition causes a less sharp decrease with increasing Pt loading and a less large spread. The particles are in this case situated on the polymer-electrolyte interface and thus contribute to a less degree to the conductivity of the electrode, when the polypyrrole layer is reduced.

Fig. 1. Ohmic resistance vs potential for a Pt electrode (●) and a PP/Pt electrode (○).

Fig. 2. Ohmic resistance vs potential curves for electrodes with various Pt loading: (a) 0.2, (b) 0.4, (c) 0.6, (d) 0.8 and (e) 1.0 $C \cdot cm^{-2}$. (1 C $\equiv$ 0.5 mg)

Fig. 3. ΔR^* vs charge used for deposition of Pt particles. For each current density the results of two series of experiments are given. Deposition current density: (A) 0.08, (B) 0.80 and (C) 8.0 $mA \cdot cm^{-2}$.

Oxidation of hydrogen [8]

The i - E curves for a rotating disc electrode, with a polypyrrole layer with electrodeposited Pt particles are shown in Fig. 4. It can be seen that a low overpotential (comparable to that of bare Pt) is needed for the oxidation of H_2 . The Levich plot in Fig. 5 shows that for a Pt loading, as low as $10 \mu g \cdot cm^{-2}$, the oxidation is (almost) only diffusion limited.

The electrodes with Pt particles, deposited during polypyrrole formation, show a much lower activity, combined with high overpotential, as can be seen from Fig. 6. The Levich plot in Fig. 7 shows that the currents are kinetically limited. This is caused by the preparation method, which yields Pt particles, covered with (poly)pyrrole. Thus only a small number of Pt sites is available for reaction.

The electrodeposition of Pt is a much more favourable method to prepare electrocatalytically active electrodes.

Fig. 4. i - E curves for a rotating Pt/PP/GC electrode with a Pt loading of $46 \mu\text{g.cm}^{-2}$ with various Pt loading: (x) 253, (---) : PP/GC electrode without Pt under the same conditions.

Fig. 5. "Levich"-plot for electrodes with various Pt loading: (x) 253, (o) 101, (□) 10 and (●) $0.05 \mu\text{g.cm}^{-2}$. (---) : results for a bare Pt electrode.

Fig. 6. i - E curves for a Pt-PP/GC electrode with a Pt loading of 24 mg.cm^{-2} . (---) : PP/GC electrode without Pt under the same conditions.

Fig. 7. "Levich"-plot for Pt-PP/GC electrodes with various Pt loading : (x) 36 mg.cm^{-2} and (o) 24 mg.cm^{-2} . (---) : results for a bare Pt electrode.

Reduction of dioxygen

The polypyrrole electrodes with incorporated Pt particles have also been used for the reduction of dioxygen in $0.5 \text{ M H}_2\text{SO}_4$. A cyclic voltammogram is shown in Fig. 8. The incorporation of Pt particles has a large influence on the overpotential and the maximum current densities. As the ring electrode is kept at a potential where the formed hydrogen peroxide is oxidized, the product composition (H_2O and/or H_2O_2) can be calculated from the ratio of the disc and ring currents. The fraction of the O_2 molecules, reduced to H_2O is shown in Fig. 9 as a function

of the Pt loading and the Pt deposition current density, at a rotating frequency of 25 Hz.

Fig. 8. Cyclic voltammograms for a Pt ring electrode and a modified disc electrode in O_2 -saturated H_2SO_4 . (---) C_p electrode with $100 \text{ mC} \cdot \text{cm}^{-2}$ polypyrrole; (—) the same electrode with $200 \text{ mC} \cdot \text{cm}^{-2}$ Pt.

Fig. 9. H_2O formation efficiency vs the Pt loading. Pt deposition current density: (●) 0.08 , (○) 0.80 and (x) $8.0 \text{ mA} \cdot \text{cm}^{-2}$.

At the electrodes with Pt particles, deposited at a high rate, dioxygen is almost completely reduced to water. Because the particles are in this case deposited mainly on the polymer/electrolyte interface, a behaviour similar to that of a bare Pt electrode is found. When the Pt particles are deposited at a lower rate (current density), the Pt particles are deposited throughout the film and less available for oxygen. Combined with a slow diffusion of oxygen into the polymer layer, this causes a reduction to hydrogen peroxide at low Pt loading. When the Pt loading is increased, more Pt sites will be available and a higher amount of O_2 is reduced to H_2O . This effect offers the opportunity to change the properties of the electrode, by variation of the preparation method.

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