Hydroquinone oxidation and p-benzoquinone reduction at polypyrrole and poly-N-methylpyrrole electrodes

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HYDROQUINONE OXIDATION AND p-BENZOQUINONE REDUCTION AT POLYPYRROLE AND POLY-N-METHYLPYRROLE ELECTRODES

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Abstract—The oxidation of hydroquinone and the reduction of p-benzoquinone in aqueous solution is studied at polypyrrole electrode and at a poly-N-methylpyrrole electrode. It is found that both types of electrodes exhibit a pronounced electrocatalytical effect. The quinone/hydroquinone redox couple, which is irreversible at an uncovered gold electrode, initially is practically reversible when a polypyrrole-covered gold electrode is used. However, after some time, an aging effect occurs, which includes an increasing inhibition of the electrode reaction by quinone-like species, immobilized at the polymer surface. Experiments with a rotating disk electrode show that the redox reactions of quinone and hydroquinone occur mainly at the interface polypyrrole/electrolyte; in this case, the polymer acts as both an electrocatalyst and an electron conductor.

NOMENCLATURE

\[ A \quad \text{area of electrode surface [m}^2\text{]} \]
\[ c \quad \text{concentration [M, mol m}^{-3}\text{]} \]
\[ D \quad \text{diffusion coefficient [m}^2\text{s}^{-1}\text{]} \]
\[ E \quad \text{potential [V]} \]
\[ E_p \quad \text{peak potential [V]} \]
\[ \Delta E_p \quad \text{peak separation [V]} \]
\[ E_{1/2} \quad \text{half-peak potential [V]} \]
\[ F \quad \text{Faraday's constant [C mol}^{-1}\text{]} \]
\[ f \quad \text{(rotation) frequency [Hz]} \]
\[ i \quad \text{current [A]} \]
\[ i_l \quad \text{limiting current [A]} \]
\[ n \quad \text{number of electrons, involved in electrode reaction} \]
\[ v \quad \text{potential scan rate [Vs}^{-1}\text{]} \]
\[ \nu \quad \text{kinematic viscosity [m}^2\text{s}^{-1}\text{]} \]

Superscripts

\[ \text{ad} \quad \text{adsorbed} \]
\[ \text{s} \quad \text{bulk} \]

1. INTRODUCTION

In previous papers[1, 2], a study of the reduction of molecular oxygen at the polypyrrole electrode was presented. These papers deal with the reaction of an inorganic substance at an organic polymer electrode. In order to study also the electrochemical reaction of an organic compound at the polypyrrole electrode, the quinone-hydroquinone system was used[3].

The oxidation of hydroquinone (or 1,4-dihydroxybenzene) and the reduction of 1,4-benzoquinone are well known redox reactions in organic electrochemistry[4].

The mechanism of these reactions in protic media, such as the electrolytes used in this study, has been established by Vetter in 1952[5]. Many publications deal with the quinone/hydroquinone redox system and some of these publications concern the polypyrrole electrode, although exclusively in aprotic electrolyte[6,7]. The measurements, carried out in a H2SO4-containing electrolyte and presented here, do not enable the determination of the mechanism of the hydroquinone oxidation and the quinone reduction at the polypyrrole electrode. However, the results lead to (sometimes speculative) conclusions that could contribute to the elucidation of this mechanism.

2. EXPERIMENTAL

The experimental set-up for the formation of the polypyrrole and poly-N-methylpyrrole films was the same as described in an earlier work[8]. Unless otherwise stated, the formation electrolyte contained 0.1 M LiClO4 (Fluka), 1 vol% pyrrole or 1 vol% N-methylpyrrole (Aldrich) and 0.5 vol% distilled water in acetonitrile (Janssen Chimica). The working electrode was a gold disk \((A = 5.15 \times 10^{-5} \text{m}^2)\), which was polished with 0.3 \(\mu\text{m}\) alumina before each deposition of the polymer film.

The cell in which the measurements were carried out was a thermostatted three-electrode cell with a saturated calomel electrode (sce) as a reference electrode and platinum foil as a counter electrode. The reference electrode was provided with a Luggin capillary and the counter electrode was separated from the working electrode compartment by a porous glass filter. The working electrode was connected to the disk circuit of a bipotentiostat (Tacussel) and its potential was controlled by a Wenking Pos 73 scan generator. After the deposition of the polymer film at a constant potential of 1.20 V vs sce, the electrode was taken out of the formation electrolyte and the excess of electrolyte was removed by spinning the electrode in ambient air. Then the electrode was dried by free standing in ambient air for about 30 min before it was transferred to the measurement cell. The charge, passed during the formation of the polymer film, was always 0.6 kC m\(^{-2}\), unless otherwise stated.

The measurements were carried out in three dif-
ferent solutions, viz (1) a solution, prepared by mixing equal volumes of 1 M \( \text{H}_2\text{SO}_4 \) in water and 96% ethanol, denoted here as \( \text{H}_2\text{SO}_4/\text{EtOH} \); (2) a solution, prepared by mixing equal volumes of 1 M \( \text{H}_2\text{SO}_4 \) in water and acetonitrile, denoted as \( \text{H}_2\text{SO}_4/\text{CH}_3\text{CN} \) and; (3) 0.5 M \( \text{H}_2\text{SO}_4 \) in water, denoted as \( \text{H}_2\text{SO}_4 \). The solutions were prepared at 293 K. The concentration of the electroactive compound, i.e. 1,4-dihydroxybenzene (hydroquinone, denoted as \( \text{H}_2\text{Q} \)) or 1,4-benzoquinone (denoted as \( Q \)), was \( 5 \times 10^{-3} \) M in each solution.

All the measurements were carried out at 298 K and 100 kPa, unless otherwise mentioned. All potentials are given against the sce.

The diffusion coefficient of \( Q \), \( D(Q) \), at 298 K in \( \text{H}_2\text{SO}_4/\text{EtOH} \) was determined by means of polaro-graphy. Using the averaged Ilkovich equation \[9\], it was found that \( D(Q) = 2.3 \times 10^{-10} \text{ m}^2 \text{s}^{-1} \) at 298 K in \( \text{H}_2\text{SO}_4/\text{EtOH} \). The kinematic viscosity, \( v \), of the \( \text{H}_2\text{SO}_4/\text{EtOH} \) solution was calculated from literature data. From the densities at 293 K of 1 M \( \text{H}_2\text{SO}_4[10] \) and EtOH[11], the composition-by-weight of the electrolyte was calculated to be 43% in EtOH. The extrapolated density of a 43% EtOH/57%H\(_2\)O mixture at 298 K is 921 kg m\(^{-3}\)[12] and its extrapolated dynamic viscosity at 298 K \( \eta = 2.39 \times 10^{-3} \text{ kg m}^{-1} \text{s}^{-1} \)[13]. This gives a kinematic viscosity \( v = 2.6 \times 10^{-6} \text{ m}^2 \text{s}^{-1} \) at 298 K.

3. RESULTS

3.1. \( \text{H}_2\text{SO}_4/\text{ethanol} \) electrolyte

The effect of covering a gold disk with a polypyrrole (PP) or a poly-N-methylpyrrole (PMP) film on the cyclic voltammogram in \( \text{H}_2\text{Q} \)-containing \( \text{H}_2\text{SO}_4/\text{EtOH} \) electrolyte is shown in Fig. 1. The somewhat broadened peaks with \( \Delta E_p \approx 200 \text{ mV} \), measured for the uncovered gold (Au) electrode, turn into narrower peaks when a PP- or PMP-covered electrode is used. For the PP(Au) electrode \( \Delta E_p \approx 50 \text{ mV} \), \( E_p - E_{p/2} = 35 \text{ mV} \) for the anodic peak and \( E_{p/2} - E_{p/3} = 40 \text{ mV} \) for the cathodic peak. For a PMP(Au) electrode \( \Delta E_p = 80 \text{ mV} \), \( E_p - E_{p/2} = 45 \text{ mV} \) for the anodic peak and \( E_{p/2} - E_{p/3} = 50 \text{ mV} \) for the cathodic peak.

For a PP film on a platinum disk, a similar effect has been found as that for the gold disk. However, the cyclic voltammogram for a platinum (Pt) electrode is obscured by a background current from the oxidation of ethanol or contaminants present in the solution, at \( E > 0.6 \text{ V} \). To avoid interference with the studied redox reaction, from now, only gold substrates were used.

A plot of the limiting current \( I_l \) vs \( \sqrt{f} \) for \( \text{H}_2\text{Q} \) oxidation (Fig. 2) shows that the slope of the straight curve is independent of the polypyrrole layer thickness and that \( I_l \) increases slightly with increasing layer thickness. The data in Fig. 2 are not corrected for background signals. It is likely that the increase of \( I_l \) for thicker polymer films is caused by oxidation of the polymer film, for which the current increases with increasing amount of polymer. A plot of \( -I_l \) vs \( \sqrt{f} \) shows nearly the same effects: practically parallel straight curves and increase of \( -I_l \), with increasing polymer layer thickness. For formation potentials between 0.9 and 1.2 V, it has been found that there is no effect of the formation potential on the \( I_l/\sqrt{f} \) curve for a PP electrode on which \( \text{H}_2\text{Q} \) is oxidized or \( Q \) is reduced.

The slope \( S_1 \) of a \( -I_l \) vs \( \sqrt{f} \) plot for the uncovered Au electrode in \( \text{H}_2\text{Q} \)-containing solution is equal to \( 2.63 \times 10^{-4} \text{ A s}^{1/2} \). Using:

\[
S = \frac{0.62 A F c^* \left[D(Q)\right]^{1/3} v^{-1/6} \sqrt{2\pi}}{A F c^* \left[D(Q)\right]^{1/3} v^{-1/6} \sqrt{2\pi}}
\]

with a disk surface area \( A = 5.15 \times 10^{-5} \text{ m}^2 \), \( D(Q) = 2.3 \times 10^{-10} \text{ m}^2 \text{s}^{-1} \), \( v = 2.6 \times 10^{-6} \text{ m}^2 \text{s}^{-1} \) and \( c^* = 5.0 \text{ mol m}^{-3} \), this gives \( n = 2.1 \).

Since the diffusion coefficient of \( \text{H}_2\text{Q} \), \( D(\text{H}_2\text{Q}) \),

\[
E_p - E_{p/2} = 40 \text{ mV}
\]

For a PMP(Au) electrode \( \Delta E_p = 80 \text{ mV} \), \( E_p - E_{p/2} = 45 \text{ mV} \) for the anodic peak and \( E_{p/2} - E_{p/3} = 50 \text{ mV} \) for the cathodic peak.

For a PP film on a platinum disk, a similar effect has been found as that for the gold disk. However, the cyclic voltammogram for a platinum (Pt) electrode is obscured by a background current from the oxidation of ethanol or contaminants present in the solution, at \( E > 0.6 \text{ V} \). To avoid interference with the studied redox reaction, from now, only gold substrates were used.

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\[
S = \frac{0.62 A F c^* \left[D(Q)\right]^{1/3} v^{-1/6} \sqrt{2\pi}}{A F c^* \left[D(Q)\right]^{1/3} v^{-1/6} \sqrt{2\pi}}
\]

with a disk surface area \( A = 5.15 \times 10^{-5} \text{ m}^2 \), \( D(Q) = 2.3 \times 10^{-10} \text{ m}^2 \text{s}^{-1} \), \( v = 2.6 \times 10^{-6} \text{ m}^2 \text{s}^{-1} \) and \( c^* = 5.0 \text{ mol m}^{-3} \), this gives \( n = 2.1 \).

Since the diffusion coefficient of \( \text{H}_2\text{Q} \), \( D(\text{H}_2\text{Q}) \),

\[
E_p - E_{p/2} = 40 \text{ mV}
\]
Hydroquinone oxidation and p-benzoquinone reduction

could not be determined polarographically, \( D(H_2Q) \) is
determined from the results of Fig. 2. The slope \( S_1 \) of
the \( I \) vs \( \sqrt{f} \) plot for the uncovered Au electrode
in
Fig. 2 is \( 2.90 \times 10^{-4} \) A s\(^{1/2}\). Taking \( n = 2 \) for both
reduction of Q and oxidation of \( H_2Q \) and using
Equation (1), it follows that \( D(H_2Q)/D(Q) = (S_1/S_2)^{1/2} \). From \( D(Q) \) and the experimental slopes
\( S_1 \) and \( S_2 \) it follows that \( D(H_2Q) = 2.7 \times 10^{-10} \) m\(^2\) s\(^{-1}\).

From Fig. 2 and a plot of \(-I_1 \) vs \( \sqrt{f} \) for the
reduction of Q, it is concluded that the oxidation of
1,4-dihydroxybenzene and the reduction of 1,4-ben-
zoquinone in \( H_2SO_4/ETOH \) electrolyte takes place at
the interface polypyrrole/electrolyte, which means
that the polypyrrole film conducts the electrons that
are involved in the redox reactions.

It is likely that when the reacting solute is
transported through the polymer film, a decrease in
limiting current with increasing film thickness should
be observed, according to a two-phase diffusion
model[14].

Plots of \( \log [I/(I_0-I)] \) vs \( E \) are given in Fig. 3 for
\( H_2Q \) oxidation and Q reduction at a PP(Au) electrode
and at an uncovered Au electrode. The currents are not
corrected for the relatively small currents due to
background processes. In the figure, the slopes of the
curves for the PP(Au) electrode are about equal to the
slopes of the corresponding curves for the uncovered
Au electrode.

Additionally, the slopes of the curves are nearly
independent of the polymer layer thickness. For the
PP(Au) electrode, the slope in Fig. 3 is 102 mV for the
\( H_2Q \) oxidation and 130 mV for the Q reduction. To
investigate the effect of aging, a PP(Au) electrode in a
\( H_2SO_4/ETOH \) solution containing \( H_2Q \), and rotated
with \( f = 10 \) Hz, is charged with a continuous triangu-
lar potential scan between 0.0 and 0.7 V with \( v = 0.010 \) V s\(^{-1}\). After 10 min, 1 h and 2 h scanning,
current/potential curves were measured at various
rotation rates. Fig. 4 shows \( I/I_0 \) at \( E = 0.70 \) V as a
function of \( 1/\sqrt{f} \). This so-called “Koutecky–Levich
plot”[15] shows that during the aging period, the \( H_2Q \)
oxidation reaction is increasingly limited by its ki-
netics, as follows from the increasing intercept of the
\( I/I_0 \) vs \( 1/\sqrt{f} \) curve at \( 1/\sqrt{f} = 0 \). For the Q reduction at
a PP electrode, a \(-I_1 \) vs \( 1/\sqrt{f} \) plot shows the same
aging effect. It appears that the magnitude of this aging
effect is less for the reduction of Q than for the
oxidation of \( H_2Q \).

For the PMP(Au) electrode, the Koutecky–Levich
plots for the oxidation of \( H_2Q \) and the reduction of Q
show that the aging effect is larger for this electrode
than for the PP electrode. For the \( H_2Q \) oxidation, for
example, the aging of the electrode, already aged for
10 min, occurs with such a high rate during the
measurements, that a bent curve is obtained in the
\( 1/I_0 \) vs \( 1/\sqrt{f} \) plot (the curve was measured with increasing
rotation frequency). For PP electrodes it has been
found that the rate of the aging process increases with
increasing temperature. Uncovered Au electrodes
show no aging effect. The aging of the PP and PMP
electrodes during \( H_2Q \) oxidation is also illustrated by
Figs 5 and 6, in which voltammograms are given at
\( f = 0 \) Hz and \( f = 16 \) Hz for each electrode. Figure 5
and cyclic voltammograms in Q-containing electrolyte
show that, in all cases, during the aging of the PP
electrode one wave occurs in the curves at \( f = 16 \) Hz.
Its height decreases with increasing aging time. Figure
6 shows that for a PMP electrode in a \( H_2Q \)-containing
solution two waves are observed in the sweep curve
at \( f = 16 \) Hz [Fig. 6(b) and (c)]. The wave at \( E = 450 \) mV for the
PMP electrode is practically in-
dependent of the aging time, while the wave at \( E = 450 \) mV decreases with increasing aging time.

The effect of water addition to the formation
electrolyte on the aging of a PP(Au) electrode is
studied for both the oxidation of $\text{H}_2\text{O}_2$ and the reduction of $\text{Q}$. The electrodes, rotated with $f = 10$ Hz, were aged for 2 h by a continuous potential sweep between 0.0 and 0.70 V with $v = 0.01$ V s$^{-1}$.

From these experiments it has been found that addition of water to the formation electrolyte retards the aging process. For example, the PP(Au) electrode, formed after addition of 5 vol % water to the formation electrolyte, shows a small aging effect for the oxidation of $\text{H}_2\text{O}_2$ and practically no aging effect for the reduction of $\text{Q}$.

The aging of a PP(Au) electrode is also studied at polymer layers of varying thickness. It is found that there is no unequivocal effect of the polymer layer thickness on the aging of the PP electrode.

3.2. $\text{H}_2\text{SO}_4$/acetonitrile electrolyte

The deposition of a PP or a PMP layer on an Au electrode has a similar effect on the cyclic voltammogram in $\text{H}_2\text{SO}_4$/CH$_3$CN electrolyte as in the $\text{H}_2\text{SO}_4$/EtOH electrolyte.

For the uncovered Au electrode in $\text{H}_2\text{SO}_4$/CH$_3$CN + $\text{H}_2\text{O}_2$, the anodic and cathodic peaks are separated
Hydroquinone oxidation and \( \rho \)-benzoquinone reduction

with \( \Delta E_p \approx 430 \text{ mV} \), which is 230 mV more than in \( \text{H}_2\text{SO}_4/\text{EtOH} + \text{H}_2\text{Q} \); \( E_p - E_{p/2} = 45 \text{ mV} \) for the anodic peak and \( E_p - E_{p/2} = 90 \text{ mV} \) for the cathodic peak. Deposition of a polypyrrole film reduces the peak separation to \( \Delta E_p \approx 70 \text{ mV} \) for a 10 min-aged electrode and \( E_p - E_{p/2} \) becomes 40 mV for the anodic peak and 45 mV for the cathodic peak. For a poly-\(-N\)-methylpyrrole film, the peak separation is \( \Delta E_p \approx 210 \text{ mV} \), with \( E_p - E_{p/2} = 70 \text{ mV} \) for the anodic peak and \( E_p - E_{p/2} = 95 \text{ mV} \) for the cathodic peak.

Generally, the behaviour of the PP and PMP electrodes in \( \text{H}_2\text{SO}_4/\text{CH}_3\text{CN} \) is analogous to the behaviour in \( \text{H}_2\text{SO}_4/\text{EtOH} \) electrolyte: the \( \text{H}_2\text{Q} \) oxidation and \( \text{Q} \) reduction occurs at the polymer/electrolyte interface; there is only a small effect of the polymer layer thickness on the \( I \) vs \( \sqrt{f} \) plot and the electrodes show also an aging effect. The aging of the PP electrode, however, occurs at a higher rate than in ethanolic electrolyte, whereas the aging rate for the PMP electrode is about equal in both electrolytes. Fig. 7 shows a plot of \( 1/I \) vs \( 1/\sqrt{f} \) for the \( \text{H}_2\text{Q} \) oxidation at an uncovered Au, PP(Au) and PMP(Au) electrode after 2 h of aging. During the aging of the PP and PMP electrodes, the cyclic voltammograms of the electrodes tend increasingly to that of the uncovered Au electrode.

The magnitude of the aging effect at a PP(Au) electrode is less for the reduction of \( \text{Q} \) than for the oxidation of \( \text{H}_2\text{Q} \). For a PMP(Au) electrode the opposite of this is found.

3.3. \( \text{H}_2\text{SO}_4 \) electrolyte

The cyclic voltammogram at an uncovered Au, a PP(Au) and a PMP(Au) electrode in \( \text{H}_2\text{SO}_4 \)-containing 0.5 M \( \text{H}_2\text{SO}_4 \) is given in Fig. 8. For the uncovered Au electrode it appears that \( \Delta E_p \approx 280 \text{ mV} \), whereas for both the PP(Au) and PMP(Au) electrodes it is found that \( \Delta E_p \approx 60 \text{ mV} \) and that for the anodic peak, \( E_p - E_{p/2} = 35 \text{ mV} \) for the PP electrode and \( E_p - E_{p/2} = 40 \text{ mV} \) for the PMP electrode. For the cathodic peak, \( E_p - E_{p/2} = 40 \text{ mV} \) for both the PP and PMP electrode. The aging effect for the various electrodes in \( \text{H}_2\text{SO}_4 + \text{H}_2\text{Q} \) electrolyte follows from Fig. 9. As for the other electrolytes, the magnitude of the aging effect is larger for the PMP electrode than for the PP electrode.

The aging effect for the uncovered Au and PP(Au) electrode in \( \text{H}_2\text{SO}_4 + \text{Q} \) electrolyte is comparable to the aging effect, shown in Fig. 9. However, for a PMP(Au) electrode, the aging effect during \( \text{Q} \) reduction is considerably larger than during \( \text{H}_2\text{Q} \) oxidation. The voltammograms recorded during the aging of a
PP(Au) electrode in H\textsubscript{2}SO\textsubscript{4} + H\textsubscript{2}Q, are similar to the voltammograms in Fig. 5. The voltammograms show one wave in the curve at $f = 16$ Hz; the height of this wave decreases with increasing aging time.

The voltammograms for the PP(Au) electrode during Q reduction are given in Fig. 10. The curves in this figure exhibit an extra anodic and cathodic peak around a potential of 0 V. These extra peaks are not caused by the presence of either H\textsubscript{2}Q or Q, but probably arise from redox reactions of the polymer film.

The aging of a PMP(Au) electrode in H\textsubscript{2}SO\textsubscript{4} + H\textsubscript{2}Q is illustrated by Fig. 11. Comparing Fig. 11(a) with Figs 11(b) and (c) suggests that the not-well-shaped wave in Fig. 11(a) actually consists of two waves, which have been split in Figs 11(b) and (c).

During the aging of the electrode, the half-wave potential $E_{1/2}$ of the second wave in the curve at $f = 16$ Hz (i.e. the wave at the most anodic potential) increases with increasing aging time, whereas the $E_{1/2}$ of the remaining first wave remains constant. The height of the second wave increases with increasing rotation frequency, while the first wave becomes increasingly independent of the rotation frequency with increasing aging time. The second wave appears as a small anodic peak in the voltammogram at $f = 0$ Hz [Figs 11(b) and 11(c)]; this small anodic peak has a small and broad cathodic counterpart [Fig. 11(c)].
When Q is reduced at a PMP electrode in 0.5 M H₂SO₄, a rapid change of the voltammogram occurs at the beginning of the experiment. The cyclic voltammogram for a PMP(Au) electrode in H₂SO₄ + Q, initially shows the well-known redox peaks with ΔEₚ ≈ 45 mV [Fig. 12(a), dashed curve]. After 30 min aging, however, the potential sweep curve is practically independent of the rotation frequency and the peak separation is reduced to ΔEₚ ≈ 30 mV [Fig. 12(a), solid curve]. After an aging period of 1 h or more, the potential sweep curve is completely independent of the rotation frequency with ΔEₚ ≈ 25 mV and Eₚ - Eₚₙ = 30 mV for the anodic peak [Figs 12(b) and (c)]. An extra pair of redox peaks develops at E = 0 V, which is similar to the results found for the PP electrode in H₂SO₄ + Q. The extra peaks at E = 0 V are also found in 0.5 M H₂SO₄ containing no Q, so they probably arise from redox reactions of the PMP film.

4. DISCUSSION

4.1. Location of the electrochemical reaction

Santhanam and O'Brien[7] studied the H₂Q oxidation at a polypyrrole electrode in anhydrous acetonitrile. It can be shown that their results are significantly affected by H₂Q, present in the polymer film at the start of the electrolysis. Consequently, their conclusion about the reaction site cannot be used for the stationary electrolysis at the limiting current.

For the polypyrrole electrode in H₂SO₄/EtOH electrolyte, the Iₓ vs ʃ/f curves in Fig. 2 and measurement in Q-containing solution show that the limiting currents are nearly independent of the polymer layer thickness and equal those at the uncovered metal. This indicates that the oxidation of H₂Q and the reduction of Q occur at the polymer/electrolyte interface.

4.2. Aging of the polymer electrodes

The PP and PMP electrodes show an aging effect in all the three electrolytes. The rate of the aging process is considerably less for the PP electrode than for the PMP electrode.

The voltammogram of the PP electrode exhibits a well-shaped wave for the H₂Q oxidation at a 10 min-aged electrode in H₂SO₄/EtOH (Fig. 5), H₂SO₄/CH₂CN and H₂SO₄. A well-shaped wave is also found for the Q reduction at a 10 min-aged PP electrode in H₂SO₄/EtOH and in H₂SO₄ (Fig. 10).

For longer aging periods, the single voltammetric wave either decreases in height (Fig. 5), or splits into two waves, of which the sum of the heights is less than the height of the original single wave for the 10 min-aged electrode (Fig. 10). The voltammogram of a PMP electrode exhibits a well-shaped wave for the oxidation of H₂Q at a 10 min-aged electrode in H₂SO₄ (Fig. 11) and for the reduction of Q at a 10 min-aged electrode in H₂SO₄/EtOH.

Taking into account the difference in rate of aging between PP and PMP electrodes, it can be concluded that for both types of electrodes similar results have been obtained. The degree of aging determines mainly the occurrence or not-occurrence of two waves.

For the Q reduction at a PMP electrode in 0.5 M H₂SO₄, the aging effect is enormous and the electrochemical response becomes that of an electrode of which the redox couple is immobilized by attachment to the electrode surface: the peaks become independent of the electrode's rotation frequency (Fig. 12).

The immobilized species will be of a quinone-like structure, since no other organic species are involved.

That some redox compound becomes immobilized during the aging of the PMP electrode in 0.5 M H₂SO₄ is also supported by the fact that ΔEₚ decreases during the aging process from ΔEₚ ≈ 45 mV after 10 min to ΔEₚ ≈ 25 mV after 1 h aging (Fig. 12). After 2 h of aging, ΔEₚ is still 25 mV, indicating that the aging process is complete and that the surface redox process is probably not completely reversible (for an ideal reversible surface redox reaction, ΔEₚ = 0[16]).

The immobilization of a redox compound during potential sweep experiments has also been observed for the H₂Q oxidation at a PP(Pt) electrode in anhydrous acetonitrile[6]. The immobilized oxidation product is identified as HQ⁺ by cyclic voltammetry and is assumed to be electrostatically bound to the polymer[6].

Since HQ⁺ is abundant in a solution of Q in 0.5M H₂SO₄ and no inhibition effect is observed without electrochemical treatment of the electrode, the immobilized compound discussed here is not HQ⁺, but presumably HQAD, which is formed by reduction of HQ⁺ according to HQ⁺ + e⁻ → HQAD. The superscript "ad" indicates that HQ is chemically or physically adsorbed.

**Fig. 12. Voltammograms of a PMP(Au) electrode in H₂SO₄ + 5.0 mM Q. v = 0.010 V s⁻¹, f = 64 Hz. Aging time: 30 min (a), 1 h (b) and 2 h (c). --- in (a): electrode aged 10 min, f = 0 Hz.**
The peaks in the cyclic voltammogram for the surface-attached species, Fig. 12, appear at about the same potentials as where the peaks were measured that corresponded to the oxidation of \( \text{H}_2\text{Q} \) and the reduction of \( \text{Q} \) when these reactions were not yet inhibited. So it is likely that the immobilized redox couple is closely related to the \( \text{H}_2\text{Q}/\text{Q} \) redox couple.

From the voltammogram in Fig. 12, it follows that an electrochemical reaction is the rate-determining step. The same aging process as for the PMP electrode in 0.5 M \( \text{H}_2\text{SO}_4 \) occurs probably for the other electrodes and electrolytes that were investigated, however, with a decreased rate.

During the aging process, the polymer electrode will become increasingly blocked by immobilized \( \text{HQ}^{\text{ad}} \) and \( \text{H}_2\text{Q}^{\text{ad}} \) species and there is a decreasing number of sites at the polymer/electrolyte interface, at which further \( \text{H}_2\text{Q} \) oxidation or \( \text{Q} \) reduction occurs. Since a decreasing part of the electrode surface is oxidizing or reducing dissolved species, a diffusion-limited anodic or cathodic current will be observed, which decreases with increasing aging time. Such an effect has indeed been found for the PP and PMP electrodes in various electrolytes: Fig. 6 clearly shows the decreasing limiting-current plateau, together with the redox peaks coming from the immobilized \( \text{H}_2\text{Q} \) and \( \text{HQ} \) species.

4.3. Electrocatalytical behaviour of the polymer electrode

The results show that the behaviour of the \( \text{H}_2\text{Q}/\text{Q} \) redox couple in aqueous acid medium is strongly affected by the deposition of a polypyrrole or a poly-(N-methylpyrrole) layer on a gold substrate. Among the three electrolytes, viz \( \text{H}_2\text{SO}_4/\text{EtOH}, \text{H}_2\text{SO}_4/\text{CH}_3\text{CN} \) and \( \text{H}_2\text{SO}_4 \), there are no large differences in the behaviour of the \( \text{H}_2\text{Q}/\text{Q} \) couple, except for the PMP(Au) electrode in \( \text{H}_2\text{SO}_4 \) electrolyte. For the last-named electrode, it appeared that, after some aging time, the voltammogram became independent of the electrode's rotation frequency (Fig. 12).

The mechanism of the hydroquinone oxidation and the quinone reduction in acid electrolyte was established by Vetter in 1952[5]. Additionally, it was found by Peters and Lingane, that platinum and gold exhibit the same chronopotentiogram in \( \text{H}_2\text{Q} \)- or \( \text{Q} \)-containing 1 M \( \text{H}_2\text{SO}_4 \)[17]. For the reduction of \( \text{Q} \) to \( \text{H}_2\text{Q} \) at a platinum electrode in aqueous electrolyte with \( \text{pH} < 5 \), the mechanism is found to be:[5]:

\[
\begin{align*}
\text{Q} + \text{H}^+ & \rightarrow \text{HQ}^+ \quad (1) \\
\text{HQ}^+ + e^- & \rightarrow \text{HQ} \quad (2) \\
\text{HQ} + \text{H}^+ & \rightarrow \text{H}_2\text{Q}^+ \quad (3) \\
\text{H}_2\text{Q}^+ + e^- & \rightarrow \text{H}_2\text{Q} \quad (4)
\end{align*}
\]

For the oxidation of \( \text{H}_2\text{Q} \) at \( \text{pH} < 5 \), the reactions (1)-(4) occur in the reverse direction[5].

From cyclic voltammograms, measured at the uncovered Au electrode (Figs 1, 8 and experiments in \( \text{H}_2\text{SO}_4/\text{CH}_3\text{CN} \) electrolyte), it is likely that the reduction of \( \text{Q} \) at an uncovered Au electrode occurs also according to the CECE mechanism, described above; the first \( E \)-step (2) will be the rate-determining step.

When a PP or a PMP film is deposited, \( \Delta E_p \) in the cyclic voltammogram considerably decreases for all the electrolytes used (Figs 1 and 8). The value of \( \Delta E_p \) mostly becomes about 60 mV, which corresponds to the \( \Delta E_p \) for a reversible one-electron reaction or for a two-electron reaction with activation polarization[18].

It is likely that \( n = 2 \) for both the \( \text{Q} \) reduction and the \( \text{H}_2\text{Q} \) oxidation at PP and PMP electrodes, since a plot of \( I \) vs \( \sqrt{f} \) shows a slope which is practically equal to the slope, found for the uncovered Au electrode (Fig. 2), for which \( n = 2 \) is obtained for the \( \text{Q} \) reduction in \( \text{H}_2\text{SO}_4/\text{EtOH} \). This means that the cyclic voltammogram at PP and PMP electrodes correspond to a two-electron reaction with some activation polarization.

The fact that the plot of \( \log[I/(I_f - I)] \) vs \( E \) for the PP and PMP electrodes shows a slope, almost equal to that observed at an uncovered Au electrode (Fig. 3), indicates that the rate-determining steps are probably the same for the three types of electrodes. Although definite conclusions about the mechanism of the \( \text{Q} \) reduction and the \( \text{H}_2\text{Q} \) oxidation cannot be drawn from the results presented here, it is likely that the mechanism of the reduction of \( \text{Q} \) to \( \text{H}_2\text{Q} \) and the oxidation of \( \text{H}_2\text{Q} \) to \( \text{Q} \) is the same at Pt, PP and PMP electrodes[reactions (1)-(4)].

The major effect of the polymer film appears to be an increase of the heterogeneous rate constant of the rate-determining reaction, viz reaction (2) for reduction and the reverse of (4) for oxidation. That the rate constants of \( \text{Q} \) reduction and \( \text{H}_2\text{Q} \) oxidation on the polymer film are higher than on gold, becomes acceptable when it is considered that, for a PP or PMP electrode, the organic molecules react on an organic electrode interface, which is likely to occur more rapidly than on a metallic electrode interface.

Irrespective of the exact nature of the effect, introduced by the polymer film, the influence of the film on the behaviour of the electrode is a good example of electrocatalysis.

REFERENCES

11. Ref.[6], p. 188.
18. Ref. [5], p. 213.