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AN ELECTROCHEMICAL AND OPTICAL INVESTIGATION OF THE ANODIC OXYGEN FILM ON PLATINUM

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE TECHNISCHE WETENSCHAPPEN AAN DE TECHNISCHE HOGESCHOOL TE EINDHOVEN, OP GEZAG VAN DE RECTOR MAGNIFICUS DR. K. POSTHUMUS, HOOGLERAAR IN DE AFDELING DER SCHEIKUNDIGE TECHNOLOGIE, VOOR EEN COMMISSIE UIT DE SENAAT TE VERDEDIGEN OP DINS Dag 25 APRIL 1967 DES NAMIDDAGS TE 4 UUR

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INTRODUCTION

Platinum metal is often used in electrochemistry work, one reason being that platinum does not readily corrode. This makes it a very suitable anode in many electrolyses. In analytical chemistry platinum is commonly used as indicator electrode.

Though many redox reactions take place at a platinum electrode in which Pt indeed acts as an electron exchange place, the potential of the electrode being solely dependent on the ratio \( \frac{c_{\text{ox}}}{c_{\text{red}}} \) of the redox couple, there are also several examples from which it is clear that Pt is involved to some extent in the reaction. Previous anodic oxidation of Pt appears to influence the kinetics of several redox reactions, e.g. the reduction of \( O_2 \) to \( H_2O \) or to \( H_2O_2 \) depends upon whether the reaction proceeds at an oxidized or at a reduced electrode.

The anodic charging curve of Pt in sulfuric acid solution shows that Pt actually behaves as an ideal condensator in a potential range of about 300 mV. Already at about 0.9 V vs H.E. the potential time curve indicates that some oxygen layer is formed on the electrode.

In this thesis it is tried to obtain more insight in this anodic film by using electrochemical and optical methods.
CHAPTER I

LITERATURE REVIEW OF THE ANODIZATION OF PLATINUM

It is generally accepted that anodization of platinum leads to a coverage with oxygen, even at potentials below the reversible potential of the reaction:

\[ 2 \text{H}_2\text{O} \xrightleftharpoons{\epsilon} \text{O}_2 + 4 \text{H}^+ + 4e^- \quad \epsilon_0 = 1.23 \text{ V} \]

Prolonged anodization or repeated anodic and cathodic treatment lowers the potential at which the oxygen coverage starts, according to ZALKIND and ERSCHLER (1-5) indicating that due to this treatment the oxygen is more strongly held at the Pt surface. It is an often raised question in what form this oxygen is present (1-1). In the literature the following pertaining observations are mentioned.

1.1. Platinum-oxide potentials

EL WAKKAD and EMARA (1-6) observed during slow anodic charging in sulfuric acid solution, two potential arrests, viz at 0.82 V and at 1.05 V vs N.H.E.. They conclude to successive formation of PtO and PtO\(_2\) because these potentials lie close to the potentials that GRUBE (1-7) and LORENTZ & SPIELMAN (1-8) found for Pt in contact with the chemically prepared oxides PtO and PtO\(_2\), namely \(\epsilon = 0.9 \text{ V}\) and \(\epsilon = 1.06 \text{ V}\) in 2 N H\(_2\)SO\(_4\). The potential of 0.9 V is an approximate value, a constant potential was not established. However this value does not seem to be very wrong because NAGEL & DIFETZ (1-3) calculated for the electrochemical formation of PtO.H\(_2\)O from Pt \(\epsilon_0 = 0.92 \text{ V}\) using THOMSON'S data for the heat of formation of this oxide.

LATIMER (1-4) gives the following potentials for the electrode reactions:

\begin{align*}
(1) & \quad \text{Pt} + 2 \text{H}_2\text{O} \xrightleftharpoons{\epsilon} \text{Pt(OH)}_2 + 2 \text{H}^+ + 2e^- \quad \epsilon_0 = 0.98 \text{ V} ; \\
(2) & \quad \text{Pt(OH)}_2 \xrightleftharpoons{\epsilon} \text{PtO}_2 + 2 \text{H}^+ + 2e^- \quad \epsilon_0 = 1.1 \text{ V} ; \\
(3) & \quad \text{PtO}_2 + \text{H}_2\text{O} \xrightleftharpoons{\epsilon} \text{PtO}_3 + 2 \text{H}^+ + 2e^- \quad \epsilon_0 = 2.0 \text{ V} .
\end{align*}
GRUBE however gives for (3)

\[ \epsilon_0 = 1.5 \text{ V} \]

1.2. Oxides of platinum

Oxides of platinum can indeed be formed during anodic oxidation: ALTMANN & BUSCH (1-9) prepared PtO\(_2\) by anodic oxidation of Pt with \( J_{\text{dc}} = 0.25 \text{ A/cm}^2 \), upon which was superimposed an alternating current, so that the total current density was 0.5 A/cm\(^2\).

They obtained PtO\(_2\) · 2H\(_2\)O in 1\% H\(_2\)SO\(_4\); PtO\(_2\) · 3-4 H\(_2\)O in 38\% H\(_2\)SO\(_4\). According to NAGEL & DIETZ (1-10) the same oxide is formed by d.c. oxidation alone with \( J = 0.1 \text{ A/cm}^2 \).

The discharge curve of this oxide flattened out at 0.8 V, from which NAGEL & DIETZ concluded that this potential corresponds with reaction (4):

\[
\text{(4) } Pt + (n+2) H_2O \rightarrow PtO_2 \cdot nH_2O + 4H^+ + 4e \quad \epsilon_0 = 0.8 \text{ V}.
\]

This implies that also the potential of reaction (2) is lower: from the potentials \( \epsilon_0 = 0.98 \text{ V} \) for reaction (1) and \( \epsilon_0 = 0.8 \text{ V} \) for reaction (4) NAGEL & DIETZ calculate \( \epsilon_0 = 0.62 \text{ V} \) for reaction (2).

TOSHIO INOUE (1-11) proved by X-ray examination that PtO\(_2\) and Pt\(_3\)O\(_4\) are formed on a Pt anode which is used for the electrochemical formation of persulfate. NAGEL & DIETZ (1-3) calculate for the Pt\(_3\)O\(_4\)-potential

\[
\text{(5) } 3Pt + 4H_2O \rightarrow Pt_3O_4 + 8H^+ + 8e \quad \epsilon_0 = 1.11 \text{ V}
\]

using ARIYA's value for the heat of formation of Pt\(_3\)O\(_4\). WOHLER (1-2) claims the formation of PtO\(_3\) · K\(_2\)O at the anode during electrolysis of a solution of PtO\(_2\) · nH\(_2\)O in KOH.

The formation of PtO\(_2\) by anodic oxidation has only indirectly been proved:

ANSON & LINGANE (1-12) dissolved the oxygen film formed by anodization of a Pt electrode in 1 N H\(_2\)SO\(_4\) for 5 min at 30 \( \mu \)A/cm\(^2\) in 0.2 M HCl and 0.1 M NaCl. Chemical analysis showed that both PtCl\(_4\)\(^-\) and PtCl\(_6\)\(^-\) were present, from which ANSON & LINGANE conclude that during anodic oxidation PtO and PtO\(_2\) are formed in the ratio 6:1.

EVERY & GRIMSLEY (1-16) oxidized Pt in KN\(_2\)O\(_3\) at 400\°C and using the same method of analysis, they also found a ratio of
6.3:1 for Pt0 and PtO₂ formation. If on top of that, Pt is oxidized with \( J = 1.1 \text{ mA/cm}^2 \) the ratio decreased to 4:2 and thus the amount of PtO₂ increased.

BREITER & WEININGER (1-13) have pointed out that these results are not a strict proof for the presence of Pt0 and PtO₂. They indicate that the results of ANSON & LINGANE equally well can be explained by a dissolution process as:

\[
\begin{align*}
(6) & \quad \text{PtO} + 2 \text{H}^+ + 2e \rightarrow \text{Pt} + \text{H}_2\text{O} \\
(7) & \quad \text{Pt} + 4 \text{Cl}^- \rightarrow \text{PtCl}_4^- + 2e \\
(8) & \quad \text{Pt} + 6 \text{Cl}^- \rightarrow \text{PtCl}_6^- + 4e
\end{align*}
\]

with \(|J_6| = |J_7 + J_8|\) (Pt0 is a formal notation here for Pt-oxide).

Summarizing it can be said that apparently PtO₂ and Pt₃O₄ are formed at high current density (0.1 A/cm² - 1 A/cm²); that Pt0 is formed at low current density (0.1 - 1 mA/cm²).

Now the platinum oxides Pt0, PtO₂ and Pt₃O₄ are also formed when Pt is heated in oxygen (1-2). Pt0 is formed at temperatures around 400°C and low oxygen pressure, PtO₂ is formed at higher temperatures. Prolonged heating at 560°C results in PtO₂- and Pt₃O₄-formation (1-14), (1-15). Anodic oxidation at low current densities appears thus to be similar to oxidation by heating in \( \text{O}_2 \) atmosphere at moderate temperatures; and anodic oxidation at high current densities to oxidation at higher temperatures.

1.3. Open circuit potentials of platinum

Although several platinum oxides have been proved to be formed, this does not necessarily imply that platinum-oxide potentials, as given by reaction 1,2 and 3 are observed indeed when the potential of anodized platinum is measured. Firstly this will depend on the exchange-current density of the platinum oxide involved. Secondly there are several redox reactions of hydrogen-oxygen compounds, which all can take place at a Pt electrode in \( \text{O}_2 \)-saturated solutions (1-4) e.g.

\[
\begin{align*}
(9) & \quad 2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4e \quad \varepsilon_\text{o} = 1.23 \text{ V} \\
(10) & \quad \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2 \text{H}^+ + 2e \quad \varepsilon_\text{o} = 0.68 \text{ V} \\
(11) & \quad \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + \text{H}^+ + e \quad \varepsilon_\text{o} = -0.13 \text{ V}
\end{align*}
\]
\( \varepsilon = 1.23 \text{ V (reaction 9) can be observed on Pt as the sole potential determining reaction, when a special pretreatment has been given; this phenomenon will be dealt with in chapter IV.} \)

A potential of 0.98 V has been reported for Pt in \( \text{O}_2 \) saturated sulfuric acid solutions (LINGANE (1-17), VISSCHER and DEVANATHAN (1-18), BIANCHI (1-19)). This platinum had been anodized and cathodized several times. This value appears to agree well with the value given by LATIMER (1-4) and by NAGEL (1-3) for reaction (1).

With respect to open circuit potentials between 0.8 and 1.1 V it should be realized that these can be due to:

a. platinum oxide potential,

b. mixed potential caused by e.g. Pt oxide and reducing impurities in the solution,

c. mixed potential caused by reactions such as (9), or (10) and reducing impurities in the solution.

SCHULDINER and ROE (1-20) have measured the dependence of the open circuit potential of Pt on \( \text{pO}_2 \) in purified 2.45 N \( \text{H}_2\text{SO}_4 \). First the electrode was kept in \( \text{H}_2 \) atmosphere (\( \varepsilon = 0 \text{ V} \)), then \( \text{H}_2 \) is replaced by He (\( \varepsilon = 0.3 \text{ V} \)). Upon introduction of oxygen the potential rises to 0.8 - 0.95 V depending on \( \text{pO}_2 \), which was varied from 0.0002 - 0.02 atm. They found:

\[
\frac{d\varepsilon}{d \log \text{pO}_2} = 0.06 \text{ V for } \text{pH} = 0 - 0.75
\]

\[
\frac{d\varepsilon}{d \log \text{pO}_2} = 0.03 \text{ V for } \text{pH} = 1.1 - 1.75
\]

According to the authors this points to the potential determining reactions (11) respectively (10).

For (11): \( \varepsilon = -0.13 - 0.059 \text{ pH} + 0.059 \log \frac{\text{pO}_2}{\text{aH}_2\text{O}_2} \)

(10) \( \varepsilon = 0.68 - 0.059 \text{ pH} + 0.030 \log \frac{\text{pO}_2}{\text{aH}_2\text{O}_2} \)

However this would mean that:

\( \text{aH}_2\text{O}_2 = 10^{-20} \text{ mol/l resp. aH}_2\text{O}_2 = 10^{-13} \text{ mol/l} \)
and it seems very unlikely that such small activities could be potential determining.

In $H_2O_2$ containing solutions ($c_{H_2O_2} = 5$ to $10^{-6}$ mol/l) BOCKRIS and OLDFIELD (1-21) measured on Pt electrode:

$$\epsilon = 0.834 - 0.059 \text{ pH independent of } pO_2.$$ Accordingly GINER found a potential of 0.81 V also independent of $pO_2$ if $c_{H_2O_2} \gg 10^{-2}$ mol/l but, if $c_{H_2O_2} \ll 10^{-4}$ mol/l, an increase of potential when the solution was saturated with $O_2$ and a decrease in $O_2$-free solutions.

BOCKRIS and OLDFIELD explain this potential value of 0.834 V by a dissociative adsorption of $H_2O_2$ on Pt

$$2 \text{Pt} + H_2O_2 \rightarrow 2(\text{Pt} - OH_{ad})$$

the potential being determined by

(12) $$\text{Pt-OH}_{ad} + H^+ + e \rightleftharpoons \text{Pt} + H_2O.$$ It may however be remarked that it has not yet been proved whether any of the intermediates as $H_0^2$ or $OH$ are actually present on the electrode surface.

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CHAPTER II

COULOMETRIC MEASUREMENT OF THE OXYGEN-COVERAGE ON PLATINUM

2.1. Literature review

2.1.1. Galvanostatic methods

The coverage of hydrogen or oxygen on platinum is most often determined by a chronopotentiometric method. In this method a galvanostatic current is applied to the Pt electrode and the potential of this electrode is recorded as a function of time. So e.g. in the case of a platinum electrode covered with adsorbed hydrogen, an anodic current is applied, which oxidizes the adsorbed hydrogen, as is indicated by a slow rise of the potential. (the potential of an electrode covered with $H_{ad}$ is of course close to $E_{rev}$). As soon as all $H_{ad}$ is ionized, the potential-time curve shows a sudden rise. The amount of electricity ($Q$) passed through up to this potential jump, is a direct measure for the quantity of $H_{ad}$ as follows from Faraday's law.

If a 1 to 1 coverage of $H$ on Pt is assumed, one can calculate from the number of Pt-atoms/cm$^2$ how many coulombs correspond with a monolayer of $H$. The number of Pt atoms/cm$^2$ depends on the crystal surface, this is for the

- (111) plane $1.5 \times 10^{15}$ atoms/cm$^2$
- (100) plane $1.3 \times 10^{15}$ atoms/cm$^2$
- (110) plane $0.93 \times 10^{15}$ atoms/cm$^2$

According to LAITINEN & ENKE (2-1) the predominant crystal face on a polycrystalline platinum surface is the (111) plane. A monolayer of hydrogen atoms on Pt corresponds thus with

$$\frac{1.5 \times 10^{15} \times 96500}{6.02 \times 10^{23}} = 2.40 \times 10^{-4} \text{ C/cm}^2$$

The coverage with oxygen is likewise derived from the potential-time curve, but now a cathodic current is applied to an oxygen-covered Pt-electrode. When the current is applied, the chrono-
potentiogram shows a quick drop in potential to about 0.9 - 0.8 V vs N.H.E.; thereafter the potential decreases slowly until the onset of the next process (coverage with hydrogen atoms), as indicated by a potential jump. With this method, often called the cathodic stripping method, the amount of electricity corresponding with the oxygen coverage, is determined. This will be named here \( Q_C \) as it is obtained by cathodic stripping.

The oxygen coverage can also be found from the charging curve, and accordingly is called here \( Q_A \). When all \( \text{H}_\text{ad} \) has been ionized, the potential rises quickly up to about 0.8 V, then due to coverage by oxygen the potential rises less rapidly until finally the steady state potential for oxygen evolution is reached. The time-interval from the onset of the oxygen-coverage till the steady state potential, multiplied by the anodic current density gives \( Q_A \). Both methods are used, but several authors found that \( Q_A \) is not always equal to \( Q_C \), this discrepancy will be discussed in section 2.1.4.

Literature data for oxygen coverage on smooth Pt are summarized in table 1 and 2. Table 1 gives \( Q_C \), obtained by stripping with a galvanostatic cathodic current density \( J_C \) when the electrode was oxidized with an anodic current density \( J_A \); also \( Q_A \) is therefore given. Table 2 gives \( Q_C \) when the electrode was potentiostatically oxidized. In these tables the roughness factor (RF) if reported, is also given. The roughness factor indicates the ratio between the electrochemical-active area of the electrode and its geometrical area.

2.1.2. The roughness factor

At first most investigators assumed that only a monolayer of oxygen would be present on platinum, so when the observed \( Q \) values turned out larger than corresponding with a monolayer, a roughness factor was introduced, which would then account for this discrepancy. Later it was realized that more than one layer could be present on the platinum surface (e.g. ERSCHLER 2-2). In more recent publications the true area of the electrode is actually determined. The surface areas that are used in these electrochemical experiments are of the order of only a few square centimeters, so gas adsorption measurements (B.E.T. method) cannot be used very well. The surface area of platinum is therefore usually established by methods that involve the measurement of the capacity of the electrode at a potential at which no electro-
Table 1  Galvanostatic oxidation and reduction of smooth Pt

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>(i_A/\text{cm}^2)</th>
<th>(Q_A)</th>
<th>(i_C/\text{cm}^2)</th>
<th>(Q_C)</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 N (\text{H}_2\text{SO}_4)</td>
<td>10 mA</td>
<td>1 mC/cm(^2)</td>
<td>0.1 mA</td>
<td>0.98 mC/cm(^2)</td>
<td>(a) A. Hickling</td>
</tr>
<tr>
<td>1 N (\text{NaOH})</td>
<td>10 mA</td>
<td>1 mC/cm(^2)</td>
<td>0.1 mA</td>
<td>0.92 mC/cm(^2)</td>
<td>(b) M. W. Breitner, C. A. Knorr</td>
</tr>
<tr>
<td>0.2 M (\text{KH}_2\text{PO}_4)</td>
<td>10 mA</td>
<td>1 mC/cm(^2)</td>
<td>1.12 mC/cm(^2)</td>
<td>0.95 mC/cm(^2)</td>
<td>(c) F. C. Anson and J. J. Lingane</td>
</tr>
<tr>
<td>0.2 M (\text{Na}_2\text{HPO}_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(2-9)</td>
</tr>
<tr>
<td>2 N (\text{H}_2\text{SO}_4)</td>
<td>2 A</td>
<td>0.77 mC/cm(^2)</td>
<td>0.1 mA</td>
<td>0.98 mC/cm(^2)</td>
<td>(d) W. Volkli</td>
</tr>
<tr>
<td>(\text{N}_2) atm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(2-3)</td>
</tr>
<tr>
<td>pH = 0</td>
<td>0.1 mA</td>
<td>1.03 mC/cm(^2)</td>
<td>0.1 mA</td>
<td>0.98 mC/cm(^2)</td>
<td>(e) K. Vetter and D. Berndt</td>
</tr>
<tr>
<td>pH = 1</td>
<td>1.18 mC/cm(^2)</td>
<td>0.92 mC/cm(^2)</td>
<td>0.95 mC/cm(^2)</td>
<td>0.95 mC/cm(^2)</td>
<td>(2-11)</td>
</tr>
<tr>
<td>pH = 4.3</td>
<td>1.30 mC/cm(^2)</td>
<td>1.08 mC/cm(^2)</td>
<td>1.32 mC/cm(^2)</td>
<td>1.32 mC/cm(^2)</td>
<td>(2-10)</td>
</tr>
<tr>
<td>pH = 6.5</td>
<td>1.39 mC/cm(^2)</td>
<td>1.19 mC/cm(^2)</td>
<td>1.19 mC/cm(^2)</td>
<td>1.19 mC/cm(^2)</td>
<td>(2-11)</td>
</tr>
<tr>
<td>pH = 8.5</td>
<td>1.22 mC/cm(^2)</td>
<td>1.19 mC/cm(^2)</td>
<td>1.19 mC/cm(^2)</td>
<td>1.19 mC/cm(^2)</td>
<td>(2-11)</td>
</tr>
<tr>
<td>pH = 10</td>
<td>1.22 mC/cm(^2)</td>
<td>1.19 mC/cm(^2)</td>
<td>1.19 mC/cm(^2)</td>
<td>1.19 mC/cm(^2)</td>
<td>(2-11)</td>
</tr>
<tr>
<td>pH ranges from 0.3 - 11.7 (\text{N}_2) atm</td>
<td>5 (\mu)A</td>
<td>2 mC/cm(^2)</td>
<td>5 (\mu)A</td>
<td>1.2 mC/cm(^2)</td>
<td>(e) K. Vetter and D. Berndt</td>
</tr>
<tr>
<td>1 N (\text{H}_2\text{SO}_4)</td>
<td>245 (\mu)A</td>
<td></td>
<td>245 (\mu)A</td>
<td></td>
<td>(g) J. Giner</td>
</tr>
<tr>
<td>(\text{He}) atm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(2-12)</td>
</tr>
<tr>
<td>1 N (\text{H}_2\text{SO}_4)</td>
<td>(10^{-7}) A</td>
<td></td>
<td>(6 \times 10^{-7}) A</td>
<td>2.5 to 8 mC/cm(^2)</td>
<td>(g) A. D. Obrucheva</td>
</tr>
<tr>
<td>(\text{NaOH})</td>
<td>(10^{-3}) A</td>
<td></td>
<td>(6 \times 10^{-7}) A</td>
<td>1.3 to 2.5 mC/cm(^2)</td>
<td>(2-13)</td>
</tr>
<tr>
<td>(\text{H}_2) atm</td>
<td>(10^{-1}) A</td>
<td></td>
<td>(6 \times 10^{-7}) A</td>
<td>1.3 to 2.5 mC/cm(^2)</td>
<td>(2-13)</td>
</tr>
<tr>
<td>(0.8 \text{ M HClO}_4)</td>
<td>0.78 (\mu)A</td>
<td></td>
<td>(122 \mu)A</td>
<td></td>
<td>(g) S. W. Feldberg, C. G. Enke, C. E. Bricker (2-15)</td>
</tr>
<tr>
<td>(\text{He}) atm</td>
<td>1 A</td>
<td>0.44 mC/cm(^2)</td>
<td></td>
<td></td>
<td>(2-14)</td>
</tr>
<tr>
<td>2 N (\text{H}_2\text{SO}_4)</td>
<td>34 (\mu)A</td>
<td></td>
<td>34 (\mu)A</td>
<td></td>
<td>(f) J. S. Mayell and S. Langer</td>
</tr>
<tr>
<td>up to 1.04 V</td>
<td>0.109 mC/cm(^2)</td>
<td></td>
<td>0.136 mC/cm(^2)</td>
<td></td>
<td>(2-16)</td>
</tr>
<tr>
<td>1.24 V</td>
<td>0.364 mC/cm(^2)</td>
<td></td>
<td>0.347 mC/cm(^2)</td>
<td></td>
<td>(2-16)</td>
</tr>
<tr>
<td>1.44 V</td>
<td>0.730 mC/cm(^2)</td>
<td></td>
<td>0.578 mC/cm(^2)</td>
<td></td>
<td>(2-16)</td>
</tr>
<tr>
<td>1.64 V</td>
<td>1.430 mC/cm(^2)</td>
<td></td>
<td>0.919 mC/cm(^2)</td>
<td></td>
<td>(2-16)</td>
</tr>
</tbody>
</table>

(a) According to Hickling only a monolayer (equivalent to 0.5 mC/cm\(^2\)) is present if RF = 2 is assumed.
(b) \(Q_A = 2 \text{ mC/cm}^2\) corresponds to a monolayer if RF = 2-3.
(c) Taking RF = 2, Giner concludes to a coverage of 0.5 mC/cm\(^2\).
(d) These values are estimated from Obrucheva’s graphical results. The Q values refer to apparent area; from Q for \(\text{NaOH}\), it follows that RF = 2. According to Obrucheva the \(Q_C\) values obtained by anodic oxidation in \(\text{H}_2\text{SO}_4\) are 3x \(Q_C\) values obtained in \(\text{NaOH}\).
(e) Determination of \(Q_A/Q_C\) see 2.1.5.
(f) From 1.04-1.54 V, \(Q_C\) is linearly dependent on potential, the slope is 1.2 mC/cm\(^2\) V\(^{-1}\).
Table 2 Potentiostatic oxidation, followed by galvanostatic reduction

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$I_C/cm^2$</th>
<th>$Q_C$</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6 N $H_2SO_4$</td>
<td>0.1 A</td>
<td>0.12 mC.cm$^{-2}$.V$^{-1}$</td>
<td>a) M. Becker and M. Breiter (2-17)</td>
</tr>
<tr>
<td>$H_2$ atm</td>
<td></td>
<td>from 0.8 to 2.1 V</td>
<td></td>
</tr>
<tr>
<td>1 N HClO$_4$</td>
<td>15 µA</td>
<td>1.0 mC.cm$^{-2}$.V$^{-1}$</td>
<td>b) H. A. Laitinen and G. C. Enke (2-1)</td>
</tr>
<tr>
<td>$N_2$ atm</td>
<td></td>
<td>from 1.05 to 1.55 V</td>
<td></td>
</tr>
<tr>
<td>2 N $H_2SO_4$</td>
<td>34 µA</td>
<td>2.16 mC.cm$^{-2}$.V$^{-1}$</td>
<td>c) J. S. Mayell and S. H. Langer (2-16)</td>
</tr>
<tr>
<td>$N_2$ atm</td>
<td></td>
<td>from 0.94 to 1.64 V</td>
<td></td>
</tr>
<tr>
<td>1 N KOH</td>
<td></td>
<td></td>
<td>c) id.</td>
</tr>
<tr>
<td>$N_2$ atm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- a) Becker and Breiter conclude to a monolayer at 1.4 V, assuming a roughness factor 1.5.
- b) $RF = 1.12$ (from adsorption measurements) has been taken into account.
- c) According to Mayell & Langer, the oxidation in alkaline solution indicates that there is a 2 electron change at 1.01 V, a 4 electron change at 1.21 V and a 6 electron change at 1.71 V ($Q_C = 1105 \mu C$), whereas in acid solution a 8 electron change was attained at 1.74 V.

Chemical reaction occurs. Measured in fact is the differential capacity of the double layer; the behaviour of an electrode being represented by a resistance and a capacitance parallel. Comparison of this capacity with the capacity ($C$) of a mercury surface, which surface is assumed to be perfectly smooth ($RF = 1$), then gives the roughness factor of the Pt-electrode (2-22). For all authors the guide for the value of $C_{Hg}$ are the papers of GRAHAME (2-21) who found a minimum value of 16 $\mu F/cm^2$ in several solutions.
(N\(\text{Na}_2\text{SO}_4\);N\(\text{NaN}_3\);N\(\text{H}_2\text{SO}_4\)). The capacity values reported in the literature for Pt-foil electrodes lie between 20 and 60 \(\mu\text{F/cm}^2\) in the potential region 0.4 - 0.8 V vs N.H.E. This corresponds with roughness factors of 1.2 - 3.8, which value of course is influenced by the treatment of the electrode (GILMAN 2-3; HOARE 2-4).

2.1.3. Potentiostatic methods

The coverage with oxygen can also be measured potentiostatically from the integrated anodic or cathodic current-time curve. In table 3 literature data are given. WILL & KNORR (2-5) have used the "triangular potential sweep" method, whereby a periodic triangular voltage is applied to the test electrode. The potential was swept between 0 and 1.6 V vs H.E. The total area under the current-potential curve is the same for the anodic and the cathodic sweep; the amount of oxygen adsorbed increases as the sweep rate decreases. Integration of the curve in steps of 120 mV shows a marked hysteresis between build up and reduction.

### Table 3  Potentiostatic oxidation and potentiostatic reduction

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>(Q_C)</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M (\text{HClO}_4)</td>
<td>1 min oxid. at 1.14 V</td>
<td>0.32 mC.cm(^{-2})</td>
</tr>
<tr>
<td>(\text{N}_2) atm</td>
<td>5 &quot;</td>
<td>0.39 &quot;</td>
</tr>
<tr>
<td>8 N (\text{H}_2\text{SO}_4)</td>
<td>Pot. sweep 1 V/sec</td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2) atm</td>
<td>Integration of anodic part: 1.1 mC.cm(^{-2}).V(^{-1}) from 1.0 to 1.6 V</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Integration of cathodic part: (Q_C) remains constant from 1.6 to 1.0 V and decreases thereafter.</td>
<td></td>
</tr>
<tr>
<td>1 N (\text{HClO}_4)</td>
<td>Electrode is kept at const. pot. during 1 sec. Integration of anodic J-t curve gives 1 mC.cm(^{-2}).V(^{-1}) from 0.8 to 1.6 V</td>
<td></td>
</tr>
<tr>
<td></td>
<td>For smaller anodization times smaller slopes for Q-(\varepsilon) curve were found. RF = 1.5, calculated from (H_{ad})</td>
<td></td>
</tr>
<tr>
<td>2.3 M (\text{H}_2\text{SO}_4)</td>
<td>Pot. sweep 1 V/sec</td>
<td></td>
</tr>
<tr>
<td>0.1 M (\text{NaOH})</td>
<td>The reported J-t graphs indicate that (Q_C) (acid soln) &gt; (Q_C) (alk.soln)</td>
<td></td>
</tr>
<tr>
<td>(\text{N}_2) atm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

19
of the oxygen layer, indicating that the reduction is a very irreversible process.

This is also obvious from the anodic and cathodic currents: the onset of the coverage reaction, as indicated by the increase of current, takes place at about 0.8 V vs H.E., the reduction is shifted in cathodic direction, a maximum is reached at about 0.9 V, depending to some extent on the sweep speed. This was likewise found by BOLD & BREITER (2-6). This irreversibility of the oxygen reduction is shown also by the hysteresis between the galvanostatic oxidation and reduction curves.

Finally the short-circuit method may be mentioned here as it is actually also a potentiostatic method. This method was used by TOOT and GRUBITSCH (2-7). The oxidized platinum electrode is connected as cathode with an unpolarizable anode, namely the Cd/CdSO₄(satd) electrode. Due to the potential difference of these two electrodes, a current flows which decreases with time. Provided that the reduction of the oxygen layer is the only process that takes place, the amount of electricity passed through is equivalent with the oxygen coverage. However the values obtained by these authors cannot be compared with those of table 3, since the oxidation process was not very well defined (exposure to air); moreover a 0.1 M NaCl solution was used in which it is known (GRUBITSCH 2-7) that part of the oxygen layer dissolves, even if the electrode is not connected with the Cd/CdSO₄(satd) electrode.

2.1.4. Comparison of the data found for the oxygen coverage

Many authors have determined Q but it should be emphasized, that reliable comparison of data is only possible if all conditions, as time of anodization, magnitude of anodic or cathodic current etc., are the same, and if the RF is determined.

Qₑ values as obtained by cathodic stripping of an electrode which was potentiostatically anodized at different potentials in the oxygen-coverage region, show a dependence of the oxygen coverage upon the potential (table 2).

Galvanostatic anodization has been carried out with high as well as with low current densities as is seen in table 1. According to VETTER & BERNDT (2-11) Qₑ is independent of current density (0.5 - 240 μA/cm²), whereas SCHULDINER & WARNER (2-14)
found a pronounced dependence for $Q_A$ on $J_A$ for currents varying from 1 mA/cm$^2$ to 1 A/cm$^2$. Lower $Q_A$ values were obtained for higher anodic current densities, which according to SCHULDINER & WARNER shows that oxygen is not only adsorbed but also absorbed. During a fast anodic current-pulse, the oxygen atoms are merely adsorbed on the metal surface; when longer charging times (i.e. low currents) are used, a large part of the deposited oxygen atoms may be absorbed into the surface of platinum.

MAYELL & LANGER (2-16) observed that, when Pt is anodized at constant potential, the value observed for $Q_C$ by cathodic stripping is larger than when this electrode was oxidized by constant current up to the same potential. E.g. they found at $1.24 \text{ V vs N.H.E.}$

$$Q_C = 660 \mu\text{C/cm}^2 \text{ at potentiostatic oxidation; but}$$
$$Q_C = 334.7 \mu\text{C/cm}^2 \text{ at galvanostatic oxidation.}$$

Since one oxygen layer corresponds with 420 $\mu\text{C/cm}^2$, they accordingly conclude that galvanostatically the value of $1.24 \text{ V}$ is not reached until the Pt surface is completely covered with PtO (or Pt(OH)$_2$); if however the electrode is oxidized potentiostatically at $1.24 \text{ V}$, the number of coulombs indicates that PtO$_2$ is formed.

However, it was shown by several authors that the anodization time affects the coulometric values, the results of MAYELL & LANGER thus suggest that with galvanostatic oxidation the steady state coverage is not yet reached. Their conclusion of PtO respectively of PtO$_2$ formation therefore seems to be rather bold.

2.1.5. The unequality of $Q_A$ and $Q_C$

Though the pattern of the anodic charging curve differs considerably from the cathodic curve, -the cathodic curve shows the more typical chronopotentiometric behaviour- both curves have been utilized for the calculation of the oxygen coverage. It appears that $Q_A$ is often larger than $Q_C$, which discrepancy, according to some authors, gives information about the mechanism of the reduction process. They conclude that because $Q_A/Q_C > 1$ the reduction is not complete. So for instance VETTER and BERNDT (2-11), who found $Q_A/Q_C = 1.5$ in 1 N H$_2$SO$_4$, suppose that the oxide is only reduced to H$_2$O$_2$, instead of to H$_2$O:

$$\text{MeO} + H^+ + e \rightarrow \text{Me} + \frac{1}{2} \text{H}_2\text{O}_2$$
This reduction scheme however could not be confirmed by SHIBATA (2-20) since he did not detect H₂O₂.

Another reduction scheme was suggested by FELDBERG, ENKE and BRICKER (2-15):

\[
\text{Pt(O)x} + x H^+ + xe \rightarrow \text{Pt(OH)x} \quad \text{fast} \\
\text{Pt(OH)x} + x H^+ + xe + \text{Pt} + xH_2O \quad \text{slow}
\]

The second reaction is assumed to proceed so slowly that this reaction does not take place during cathodic stripping. FELDBERG c.s. come to this conclusion because they observed that potentiostatic anodization in 0.8 M HClO₄ for 2 min at 1.40 V vs H.E., followed by cathodization at constant current (122 μA/cm²), gives a ratio \(Q_A/Q_C\) which depends upon the time that the electrode was kept at a potential of 0.6 V before being anodized. As \(Q_C\) remained constant, this pretreatment at 0.6 V thus results in higher \(Q_A\) values. A maximum value \(Q_A = 2\ Q_C\) was obtained when the electrode had been kept at 0.6 V during 3 hours. According to FELDBERG c.s. this implies that then the oxidation was started on a really clean or reduced electrode. The same results were found if the oxidation was performed with constant current.

Quite another explanation for the inequality of \(Q_A\) and \(Q_C\) was given by MAYELL & LANGER (2-16). They reported that in 2N H₂SO₄ up to 1.24 V vs N.H.E. the number of coulombs used for galvanostatic oxidation is equal to the number of coulombs needed for galvanostatic reduction, but \(Q_A > Q_C\) for potentials more anodic than 1.24 V. They ascribe the excess of \(Q_A\) to be due to another reaction such as oxidation of H₂O to O₂. Now side reactions (e.g. oxidation of impurities) could also be the reason why FELDBERG found increasing \(Q_A/Q_C\) ratio's with prolonged pretreatment at 0.6 V. Indeed if they kept the electrode at 0.5 V before oxidation, the ratio \(Q_A/Q_C\) even increased to 3. The authors supposed that only ratio's of \(Q_A/Q_C\) greater than 2 are due to impurities.

2.2. Experimental determination of the oxygen coverage

The chronopotentiometric method was used to determine the oxygen coverage on Pt in 0.25 M H₂SO₄ and in 0.1 M NaOH solutions. The platinum was potentiostatically oxidized.

In order to establish whether at a given potential the coulometric measurements depend on the cathodic current-density, \(Q_C\) was measured as a function of current density.
The electrochemical active area of the Pt electrode was calculated from its capacity value as determined by the potentiostatic pulse method.

2.2.1 The cell

The Pt electrode was a smooth platinum foil of 2.0 cm² geometric area, spotwelded to a Pt-wire which was sealed in a pyrex glass support. The counter electrode was also a Pt-electrode (area 5 cm²). Reference-electrode was a Pt-hydrogen electrode in the same solution. The anode- and cathode compartments of the cell were separated by a glass filter. Oxygen-free N₂-gas was passed through the solution. 0.25 M H₂SO₄ was prepared from p.a. H₂SO₄ and twice distilled H₂O. 0.1 M NaOH was prepared by electrolysis of p.a. NaOH solution at a mercury cathode; the sodium-amalgam was washed and then decomposed with twice distilled water to the desired NaOH concentration.

Procedure

With a Wenking potentiostat the test electrode was kept at the required anodic potential for 15 min. Then the potentiostatic circuit was cut off and a cathodic galvanostatic current was imposed on the electrode. This was done by means of a fast switch: a mercury wetted contact relay Elliott type EB 2 A 1516. (Fig. 2-1 and 2-2).

![Figure 2-1](image-url)

**Fig. 2-1** Block diagram of the apparatus for coulometric measurements.
The potential was observed on a Keithley tubevoltmeter and recorded as a function of time with a Sargent recorder. For currents higher than 250 $\mu$A/cm$^2$ the potential-time curves were photographed from the screen of a Tektronix oscilloscope with a Polaroid camera. $Q_c$ is calculated from the transition time (inflection point 0.4 - 0.3 V), as obtained from the potential-time curves (fig. 2-3).

Unless otherwise mentioned all data are given with respect to the geometrical area.
2.2.2 Variation of the cathodic density

The Pt-test electrode was kept at 1.40 V vs. H.E.; the electrolyte was 0.1 M NaOH. The current density was varied from 0.65 µA/cm² to 50 mA/cm².

The results are plotted in fig. 2-4. The graph shows that \( Q_C \) is constant for currents \( > 10 \mu A/cm^2 \).

![Graph showing dependence of \( Q_C \) on cathodic current density]

Fig. 2-4 Dependence of \( Q_C \) on cathodic current density.
Electrolyte: 0.1 M NaOH.

2.2.3 Dependence of the oxygen coverage on anodic potential

The Pt-test electrode was oxidized at various potentials in the region 0.90 - 1.70 V vs H.E.

\( Q_C \) was determined in 0.25 M \( H_2SO_4 \) with \( J_C = 52.5 \mu A/cm^2 \) and in 0.1 M NaOH with \( J_C = 46.0 \mu A/cm^2 \). The results are plotted in fig. 2-5 and 2-6. In both electrolytes a linear dependence of the oxygen coverage with potential is observed.

The slope of the curves \( Q_C \) vs potential is

- in 0.25 M \( H_2SO_4 \) \( 1.70 \text{ mC.cm}^{-2} \cdot \text{V}^{-1} \)
- in 0.1 M NaOH \( 1.18 \text{ mC.cm}^{-2} \cdot \text{V}^{-1} \)
Fig. 2-5  Dependence of $Q_C$ on anodic potential.
Electrolyte: 0.25 M H$_2$SO$_4$.

Fig. 2-6  Dependence of $Q_C$ on anodic potential.
Electrolyte: 0.1 M NaOH.

2.2.4 The determination of the real surface area

The real area of the Pt electrode at which the oxygen coverage measurements were performed, was calculated from its capacity value. This was determined with the potentiostatic pulse method (BERNDT 2-23).
Square wave potential pulses of 20 mV are applied to the test electrode which was kept at various controlled potentials in 0.25 M H₂SO₄, through which O₂-free N₂ gas was passed. The current, measured as the voltage drop over a resistance of 200 Ω, was observed as a function of time with a Tektronix oscilloscope and photographed from the screen with a Polaroid camera. At each potential the capacity is found from the integrated potential-time curve and the potentiostatic pulse. Fig. 2-7 gives a diagram of the equipment.

The results are plotted in fig. 2-8. It is seen that the capacity is constant over the potential range 0.2 - 1.0 V, after which a sharp rise occurs around 1.1 V, (as was likewise observed by LAITINEN & ENKE (2-1); SCHULDINER & ROE (2-24)). The resulting value of C is 30 μF/cm², the roughness factor is then

\[
\frac{C_{Pt}}{C_{Hg}} = \frac{30}{16} = 1.88
\]
2.3. Discussion

a. It follows from 2.1.1 that a monolayer of oxygen on a smooth surface corresponds to 0.480 mC/cm². Taking into account the roughness factor of 1.88, as established in 2.2.4 a monolayer of oxygen corresponds here to 0.902 mC/cm². From fig. 2-4 it follows that a monolayer is reached at a potential of 1.40 V. This is also concluded by BECKER & BREITER (2-17), HOARE (2-25).

MAYELL & LANGER (2-16) argue that potentiostatic oxidation leads to formation of a monolayer PtO at 1.14 V (Q=0.405 mC/cm²) and to PtO₂ at 1.24 - 1.34 V (Q=0.660 - 0.866 mC/cm²). However they have not taken into account a roughness factor.

b. The oxygen-coverage increases linearly with potential (fig. 2-4). Taking into account the roughness factor the observed slope in 0.25 M H₂SO₄ is 0.90 mC.cm⁻².V⁻¹.

c. In 0.1 M NaOH solution the slope of Qc vs potential appears to be smaller: 0.63 mC.cm⁻².V⁻¹.

As can be seen from the tables 1 and 2, some authors found no dependence on pH for the oxygen coverage; OBRUCHEVA (2-13) and MAYELL & LANGER (2-16) found lower values in alkaline solutions.
d. Finally it may be said that these coulometric measurements only give information about the amount of oxygen on platinum. No conclusion can be drawn about the form, oxide or adsorbed oxygen, in which this oxygen is present.

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CHAPTER III

CURRENT TIME BEHAVIOUR AT ANODIC POTENTIALS

3.1. Introduction

An anodic current is observed at potentials below the potential of about 1.7 V vs H.E. at which oxygen evolution at platinum becomes visible.

In this potential region (1.0 - 1.6 V vs H.E.) platinum is covered with an oxygen film as was shown in chapter II. The anodic current flowing through the system when Pt is held at potentials between 1.0 and 1.7 V is therefore to be associated with the anodic process whereby this oxygen coverage is built up. As it was found that there is no anodic dissolution of Pt in M \( \text{H}_2\text{SO}_4 \) or M NaOH, no corrosion current has to be taken into account.

T.P. HOAR (3-1) measured this I-t behaviour at 1.23 V: the current appears to decay with \( t^{-\frac{1}{2}} \) and this is explained by HOAR as a filling up process of the pores of the oxygen film. LAITINEN and ENKE (3-2) observed I-t curves for anodic polarization at 1.25 V up to 1.65 V in 0.1 M \( \text{H}_2\text{SO}_4 \); they also found I proportional to \( t^{-\frac{1}{2}} \), but they suppose a diffusion of oxygen atoms into platinum. A kinetic relation I \( \propto t^{-1} \) was derived by FELDBERG, ENKE and BRICKER (3-3) and also by GILMAN (3-4) for the same potential region. FELDBERG c.s. derived from this I \( \propto t^{-1} \) relation, that Q \( \propto \log t \) and they showed that the data of LAITINEN and ENKE obey that relation.

3.2. Experimental

In order to evaluate the current-time relationship, potentiostatic experiments were carried out. The Pt-test electrode - a Pt foil of 2 cm\(^2\) area - is kept at a constant potential of 0.3 or 0.4 V; at this potential the surface is oxygen free as was shown in chapter II. It is then quickly brought to a higher potential \( \varepsilon_H^* \) by means of a micro-switch. (fig. 3-1).
The current is followed as the voltage drop over a resistance of 10 Ω and is registered as a function of time on a recorder or a galvanometer. This was done for various \( \epsilon^* \)-values.

All potentials were measured with respect to a Pt hydrogen electrode in the same solution.

The measurements were carried out in 0.25 M \( \text{H}_2\text{SO}_4 \) and in 0.1 M \( \text{NaOH} \); \( \text{O}_2 \)-free \( \text{N}_2 \) gas was passed through. These solutions were prepared from p.a \( \text{H}_2\text{SO}_4 \) respectively from freshly electrolyzed sodium amalgam, with twice distilled water.

3.3. Results

The current-time plots show 2 types of behaviour depending on the value of the potential \( \epsilon^* \).

For \( \epsilon^* = 1.2, 1.4 \) and 1.6 V a straight line is obtained when \( J \) versus \( t^{-1} \) is plotted (figures 3-2,3,4,5,6,7).
Fig. 3-3 Plot of $J$ vs $t^{-1}$ at 1.4 V in 0.25 M H$_2$SO$_4$.  

Fig. 3-4 Plot of $J$ vs $t^{-1}$ at 1.6 V in 0.25 M H$_2$SO$_4$.  

CURRENT-DENSITY, $\mu$A/cm$^2$
Fig. 3-5 Plot of J vs $t^{-1}$ at 1.2 V in 0.1 M NaOH.

Fig. 3-6 Plot of J vs $t^{-1}$ at 1.4 V in 0.1 M NaOH.
Fig. 3-7 Plot of $J$ vs $t^{-1}$ at 1.6 V in 0.1 M NaOH.

For $E^*_H = 1.8$ V a linear relation $J - t^{-\frac{1}{2}}$ is found (fig. 3-8,9).

Fig. 3-8 Plot of $J$ vs $t^{-\frac{1}{2}}$ at 1.8 V in 0.25 M $H_2SO_4$. 
3.4. Discussion

3.4.1 The J-t\(^{-1}\) relation

If during the discharge step in the anodic reaction, the intermediate is adsorbed on the electrode surface, it is clear that this adsorbate can affect the rate of the discharge process. This problem has been dealt with by TEMKIN (3-5; 3-6). He based his theory on the experimentally established fact that the heat of adsorption decreases with increase of coverage for intermediate values of \(\theta\) (\(\theta = \text{fractional coverage } 0.2 < \theta < 0.8\)). This has also been found for the adsorption of gaseous oxygen on Pt (BRENNAN, HAYWARD and TRAPNELL (3-7)). TEMKIN assumes that the standard free energy of adsorption likewise changes with coverage according to

\[
\Delta G_\theta^O = \Delta G_0^O + f_1 RT \theta
\]

in which \(\Delta G_0^O\) and \(\Delta G_\theta^O\) are the standard free energy of adsorption at coverage \(\theta\) and on the free surface \((\theta = 0)\), \(f_1\) is a proportionality factor. \(f_1\) is positive if the exothermic free energy of adsorption is negative.
TEMKIN showed that the change in $\Delta G_0$ should be accompanied by a proportional change in the standard free energy of activation. The rate equation for the anodic reaction can then be written (3-6) as

\[ J = k_A \text{cre}_\text{rd} \exp \left( -\frac{\Delta G_0^* + \gamma f \theta R T}{RT} \right) \] in which $k_A =$ specific rate constant for the anodic reaction, $c_{\text{red}} =$ concentration of $\text{H}_2\text{O}$ or $\text{OH}^-$, $\Delta G_0^* =$ apparent standard free energy of activation for the adsorption at the uncovered surface, $\gamma =$ symmetry factor $0 < \gamma < 1$. Usually $\gamma = 1 - \alpha$ in which $\alpha =$ symmetry factor for the discharge step.

Writing $k'_A = k_A \exp \left( -\frac{\Delta G_0^*}{RT} \right)$ then gives for (2):

\[ \text{J} = k'_A c_{\text{red}} \exp \left( -\gamma f \theta \right) \exp \left( \frac{\alpha n F e}{RT} \right) \]

When a constant potential is applied to the electrode, the current decreases with time.

This time variation can be derived from eq. (3). If for $J$ is written $Q_M \frac{d\theta}{dt}$, with $Q_M =$ number of coulombs required for one monolayer of oxygen, it follows

\[ Q_M \exp \gamma f \theta \frac{d\theta}{dt} = k'_A \text{cre}_\text{rd} \exp \left( \frac{\alpha n F e}{RT} \right) \]

and integration gives

\[ \frac{Q_M}{\gamma f} \exp \gamma f \theta = k'_A c_{\text{red}} t \exp \left( \frac{\alpha n F e}{RT} \right) + A \]

The integration constant can be derived from the boundary condition $t = 0 \theta = 0$, thus $A = \frac{Q_M}{\gamma f}$. Substituting this in (4) and taking the logarithm:

\[ \ln \left( \frac{Q_M}{\gamma f} \exp \gamma f \theta \right) = \ln \left[ k'_A c_{\text{red}} t \frac{\gamma f}{Q_M} \exp \left( \frac{\alpha n F e}{RT} \right) \frac{\gamma f}{\gamma f} + 1 \right] \]

If $1$ may be neglected with respect to $k'_A c_{\text{red}} t \frac{\gamma f}{Q_M} \exp \left( \frac{\alpha n F e}{RT} \right)$, that is to say when $t$ is not too small, differentiation gives:

\[ \gamma f \frac{d\theta}{dt} = \frac{1}{t} \]

or

\[ J = \frac{Q_M}{\gamma f} \cdot \frac{1}{t} \]

A linear relation $J$ vs $t^{-1}$ was indeed found for $c^*_H = 1.2 \text{ V}, 1.4 \text{ V}$ and $1.6 \text{ V}$ in $0.25 \text{ M H}_2\text{SO}_4$ as well as in $0.1 \text{ M NaOH}$. The slope of the curve $J-t^{-1}$ must be equal to $Q_M/\gamma f$. Now in chapter II it was found that $Q_M = 0.9 \text{ mC/cm}^2$. If for the factor $\gamma$ the usual value
is taken, then $f$ can be calculated from the observed slopes. The resulting values are:

\[
\begin{align*}
\text{in } 0.25 \text{ M } H_2SO_4 & \quad \text{in } 0.1 \text{ M } NaOH \\
\varepsilon^*_H &= 1.2 \quad 1.4 \quad 1.6 \text{ V} & \varepsilon^*_H &= 1.2 \quad 1.4 \quad 1.6 \text{ V} \\
f &= 10 \quad 9 \quad 6 & f &= 13 \quad 10 \quad 12
\end{align*}
\]

These values are of the same order of magnitude as given by GILEADI (3-5) for other electrochemical reactions.

In order to check the validity of the assumption

\[
k_A \text{ c}_{\text{red}} t \frac{\gamma f}{Q_M} \exp \frac{\alpha n F \varepsilon}{R T} \gg 1
\]

we substituted $f = 10$. Calculation shows that this is true for $t > 0.1 \text{ sec}$.

Because indeed a $J - t^{-1}$ behaviour is observed, we can conclude that the first build-up of the anodic film is described by a "TEMKIN" relation. This relation is based on the assumption that the free energy of activation $\Delta G^*_\theta$ increases with $\theta$.

\[
\Delta G^*_\theta = \Delta G^*_0 + \gamma f R T \theta
\]

$f$ appears to be smaller in acid solution than in alkaline solution. This means that the rate of increase of $\Delta G^*_\theta$ with $\theta$ is less in acid solution. Increasing coverage thus affects the velocity of the reaction more in alkaline solution, than in acid solution.

Though according to TEMKIN, both $\Delta G^*_\theta$ and $\Delta G^*_0$ will increase with $\theta$, the rate of increase with $\theta$ is not necessarily the same. But it is likely that also $\frac{d\Delta G^*_\theta}{d\theta}$ will be smaller in acid solution than in alkaline solution. With $\Delta G$ proportional to $\varepsilon$, it is thus to be expected that

\[
\frac{d\varepsilon}{d\theta} \text{ in } 0.25 \text{ M } H_2SO_4 \text{ is smaller than } \frac{d\varepsilon}{d\theta} \text{ in } 0.1 \text{ M } NaOH.
\]

In chapter II we have determined the rate of increase of $\theta$ with $\varepsilon$; from these we calculate

\[
\begin{align*}
\frac{d\varepsilon}{d\theta} &= 0.53 \text{ in } 0.25 \text{ M } H_2SO_4 \\
\frac{d\varepsilon}{d\theta} &= 0.76 \text{ in } 0.1 \text{ M } NaOH
\end{align*}
\]
thus indeed a smaller value in 0.25 M $\text{H}_2\text{SO}_4$. We can say therefore that the fact that the rate of increase of coverage with potential is higher in acid solution than in alkaline solution is due to a smaller decrease of heat of adsorption with coverage in the former.

The smaller $f$ value at 1.6 V in sulfuric acid solution indicates that here $\Delta G_{\theta}$ is less dependent on $\theta$. For high coverage this is to be expected since generally the rate of decrease of the heat of adsorption with coverage becomes smaller at high coverages (TRAPNELL (3-8)).

3.4.2 The $J-t^{-\frac{1}{2}}$ relation

For $\epsilon_H^* = 1.8$ V the current time relation appears to obey a $J-t^{-\frac{1}{2}}$ law. Part of this current is due to the oxygen evolution reaction. If we assume that this $\text{H}_2\text{O}$-oxidation current is not time-dependent, then the Pt-oxidation current appears to be

$$J_{\text{ox}} = B_1 t^{-\frac{1}{2}} \quad \text{or} \quad \frac{\Delta Q}{\Delta t} = B_1 t^{-\frac{1}{2}} \quad \text{and} \quad Q = B_1 t^{\frac{1}{2}}$$

$B_1,2$ = constant.

This kinetic relation indicates that diffusion takes place through the intervening oxygen layer.

According to FICK's diffusion law:

$$\frac{\Delta c}{\Delta L} = \frac{3}{3L} \quad D \frac{\Delta c}{\Delta L}$$

$L$ = thickness of the layer

$D$ = diffusion coefficient

$\frac{\Delta c}{\Delta L}$ = concentration gradient in the layer.

This can be written as (3-16)

$$J = nF \Delta c \sqrt{\frac{D}{\pi t}}$$

Substituting for $c$ the surface concentration, a value of $D=10^{-15}$ cm$^{-2}$ sec is calculated. This low value does not seem improbable for the diffusion coefficient.

Whether the attack of the metal takes place preferentially along the grain boundaries, has not been established unambiguously. DAVIS (3-9) observed a darkening of the grain boundaries, but MOHLINER, ARGERSINGER and ADAMS (3-10) strongly doubt this. KALISH and BURSHEIN (3-11) have shown that diffusion of oxygen from the interior to the surface can take place; LUK'YANCHEVA and BAGOTSKY (3-12) conclude from oxygen adsorption measurements on degassed Pt in 1 N $\text{H}_2\text{SO}_4$ that some $O_{\text{ad}}$ penetrates into the platinum.
This diffusion process takes place after the surface is about completely covered by oxygen. Now a monolayer is formed at about 1.40 V and a deviation of the J-t\(^{-1}\) is observed indeed at 1.60 V for large values of t.

A similar behaviour has been reported for the adsorption of gaseous O\(_2\) on Pt.

In the temperature range 20-400°C the oxygen uptake is at first very rapid, thereafter the uptake proceeds relatively slow. WEISS-MANTEL, SCHWABE and HECHT (3-13) found for the first uptake

\[ g = b_1 \log (k_1 t + 1) \]

and for the subsequent slow uptake

\[ g = b_2 t^{1/m} \]

\( g \) = amount of oxygen
\( b_1 \) and \( b_2 \) are constants
\( 1/m \) is a function of temperature; at 300°C \( 1/m = 0.25 \).

At high temperatures (400°C) the first uptake appears to be too quick to be detected.

ANDRUSHENKO and SHISHAKOV (3-14) observed the same relation for the slow uptake, with \( 1/m = 0.25 \); for the first uptake they measured \( g = (1 - e^{-t/2}) \).

MIGAL and TSIPILYAKOVA (3-15) determined the adsorption of gaseous O\(_2\) on Pt in 0.1 M H\(_2\)SO\(_4\). They likewise found \( g = b_2 t^{1/m} \).

From their graphical results a value of 0.4 for \( 1/m \) can be calculated.

The equation \( g = b_1 \log (k_1 t + 1) \) is the same as given in eq. (5) and this implies that the first uptake of gaseous oxygen also can be described by a TEMKIN relation.

This first uptake appears thus to be similar to the electrochemical process at 1.2, 1.4 and 1.6 V, whereas the slow uptake of gaseous O\(_2\) shows a similarity with the electrochemical reaction at 1.8 V, this probably being diffusion controlled.

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CHAPTER IV

THE REVERSIBLE POTENTIAL OF THE REACTION \(2H_2O \rightarrow O_2 + 4H^+ + 4e\)

4.1. Introduction

A very low exchange current density has been found for the reaction

\[2H_2O \rightarrow O_2 + 4H^+ + 4e\]

in sulfuric acid solution: \(J_0 = 2.10^{-10} \text{ A/cm}^2\) \(4-2, 4\)

This value is obtained by extrapolation of the anodic Tafel line (potential versus log. current density) to 1.23 V. Because of this low \(J_0\) value, an open circuit potential of 1.23 V will therefore not always be observed on a Pt electrode in \(O_2\)-saturated solution; any reaction with \(J_0 > J_{O_2}H_2O\) will interfere, e.g. oxidation of impurities, reactions of Pt with \(O_2\); the result being that most often on Pt, potentials below 1.23 V are measured \(4-1\).

Notwithstanding these difficulties, the reversible \(O_2\) potential actually has been observed on Pt. This was for the first time reported by BOCKRIS and HUQ \(4-2\) and was later repeated by WATANABE and DEVANATHAN \(4-3\) and by VISSCHER and DEVANATHAN \(4-4\) in dilute sulfuric acid solutions.

BOCKRIS and HUQ observed \(\epsilon_H = 1.24 \pm 0.03 \text{ V in } 0.01 \text{ N } H_2SO_4\) on Pt electrodes that had been heated at 500°C in \(O_2\) atmosphere for 2 hours. The electrodes were kept in \(O_2\) atmosphere while the electrolyte was being purified by cathodic pre-electrolysis for 24 hours, followed by anodic pre-electrolysis during 48 hours on an auxiliary electrode. This potential was also observed when the rate of \(O_2\) evolution was measured as a function of potential and the current was switched off at very low current densities.

WATANABE and DEVANATHAN measured \(\epsilon_H = 1.23 \pm 0.02 \text{ V on Pt electrodes that had been given an anodic treatment}(\text{J}=10^{-4}-10^{-2}\text{A/cm}^2)\), followed by exposure to \(O_2\) while the solution was purified by anodic pre-electrolysis, this was confirmed by VISSCHER and DEVANATHAN.
When Pt is soaked for 72 hours in conc. HNO₃ and then immersed in pre-electrolyzed 2N H₂SO₄, HOARE (4-5) found an open circuit potential of 1.17 V vs Pd-H electrode. This potential is converted to N.H.E. by adding 47 mV, so this HNO₃ treatment likewise results in the reversible potential.

In alkaline solutions the reversible potential has not been reported as yet.

4.2. Experimental

4.2.1. Cell

The measurements of the open circuit potentials were carried out in a cell, consisting of three compartments separated by water-sealed taps (fig.4-1). These taps were closed during pre-electrolysis and potential measurements; the thin liquid film around the tap enables sufficient electrolytic conduction. In the first compartment a counterelectrode (Pt-foil) was placed; the middle compartment was closed by a cap, which could contain several test electrodes. These test electrodes consisted of Pt foil of 2 cm², spotwelded to Pt wire and sealed in pyrex glass supports.

Fig. 4-1 Cell

1-Reference-electrode; 2-Test-electrode; 3-Counter-electrode.
All potentials were measured against a Pt-H₂ reference-electrode, which was placed in the third compartment and in the same solution.
The hydrogen gas was purified by passing through a purification train filled successively with silicagel, NaOH beads, Cu (heated to 450°C), platinized asbestos (kept at 200°C) and silicagel. The electrolytes were 0.25 M H₂SO₄ and 0.1 M NaOH, both prepared from p.a. chemicals and twice distilled water. Anodic pre-electrolysis was carried out with an auxiliary Pt electrode (J = 5-10 mA/cm²).

4.2.2 Procedure

The test electrodes were repeatedly anodized and cathodized outside the cell before being used. Thereafter the test electrodes were washed successively with hot chromic sulfuric acid, concentrated sulfuric acid and finally with twice distilled water. The electrodes were assembled in the cap of the anode compartment and inserted in the cell where each was oxidized with J = 2 mA/cm² during 1 hour. The electrodes were thereafter raised above the solution and kept in O₂ atmosphere above the solution, while the electrolyte is pre-electrolyzed with an auxiliary electrode for 20 hours. The O₂ gas is purified by passing through a purification train, packed successively with silicagel, platinized asbestos (kept at 200°C), NaOH beads and silicagel. After pre-electrolysis, the electrodes were immersed in the solution and the potentials were measured with a Philips tubevoltmeter GM 6020, input impedance 100 MΩ.

4.3 Results

4.3.1 Measurements in 0.25 M H₂SO₄

Upon immersing in the solution that was saturated with oxygen the following potentials were observed:

Electrode A : εₗ = 1.22 V ; 1.21 V ; 1.22 V
Electrode B : εₗ = 1.24 V
Electrode C : εₗ = 1.26 V
Electrode D : εₗ = 1.22 V ; 1.26 V
Electrode D was a platinized Pt electrode.

The dependence of this observed potential on oxygen pressure was established by dilution of the O₂ gas stream with N₂:
Electrode C

| 100% O₂ | ε_H = 1.260 V |
| 99.65% N₂ + 0.35% O₂ | ε_H = 1.230 V |

a decrease in potential of 0.030 V.

According to the Nernst relation the dependence of the potential of the reaction (1) on the oxygen pressure is given by

$$\frac{d \varepsilon}{d \log p_{O₂}} = \frac{0.059}{4} \ V$$

This results in an expected decrease of 0.036 V. The observed decrease may be regarded to be in sufficient agreement with this value to conclude that the reversible potential indeed was established.

4.3.2 Measurements in 0.1 M NaOH

In 0.1 M NaOH the potentials observed when the electrode is immersed in the solution are:

Electrode A : ε_H = 1.250 V ; 1.245 V
Electrode B : ε_H = 1.24 V ; 1.25 V ; 1.25 V
Electrode C : ε_H = 1.24 V
Electrode D : ε_H = 1.22 V ; 1.24 V ; 1.21 V

O₂-pressure effect was established for electrode B:

| 100% O₂ | ε_H = 1.250 V |
| 96% N₂ + 4% O₂ | ε_H = 1.225 V |
| 100% O₂ | ε_H = 1.250 V |

This also fairly agrees with the expected decrease of potential of 0.021 V.

Fig. 4-2 Effect of O₂-pressure on the potential of a smooth Pt electrode. Electrolyte: 0.1 M NaOH.
One electrode was treated as reported by HOARE (72 hours soaking in conc. HNO₃), thereafter the electrode was washed with twice distilled water, inserted in the anode cap and kept in O₂-atmosphere during pre-electrolysis of the solution. The potential measured was 1.25 V in 0.1 M NaOH.

4.4. Influence of pretreatment

These potentials were measured immediately or soon after the electrode was immersed in the solution. If however the potential is measured after the anodic current is switched off, thus without raising the electrode above the solution, then the potential decays only very slowly to 1.24 V. Since this decay takes a rather long time, impurities might diffuse to the electrode and interfere. This seems to be indicated by the fact that after about 15 hours this potential had decreased from 1.24 to 1.18 V. The electrode was now raised above the solution and the solution was pre-electrolyzed for 20 hours. When this electrode then again was immersed in the solution, the potential rose from 1.17 V to 1.24 V in 30 min.

The advantage of the O₂ treatment (i.e. anodic oxidation followed by exposure to oxygen atmosphere) is that the potential of the reaction 2 H₂O + O₂ + 4H⁺ + 4e is established soon after the immersion of the electrode in the solution.

In order to determine what is most crucial in this treatment, the following experiments were performed in 0.25 M H₂SO₄:

a- Electodes anodized and raised above the solution.
Pre-electrolysis 20 hrs, no O₂ gas was passed through. Half an hour before the electrodes were immersed in the solution, O₂ gas is passed through. The observed potentials were: electrode E $\epsilon_H = 1.11$ V, electrode F $\epsilon_H = 1.10$ V. The same electrodes were again anodized and raised above the solution, pre-electrolysis 15 hrs, O₂ gas was passed through. After immersing in the solution the potentials: electrode E $\epsilon_H = 1.22$ V, electrode F $\epsilon_H = 1.23$ V were immediately observed.

b- Electrode E anodized and raised above the solution.
Pre-electrolysis 20 hrs, N₂ gas was passed above the solution. Half an hour before the electrode is immersed in the solution O₂ gas is passed through. The observed potential was $\epsilon_H = 1.15$ V. The same electrode was anodized, and raised above the solution. Pre-
electrolysis 20 hrs, \( O_2 \) gas was passed through. Upon immersing in the solution a potential of 1.24 V was observed.

c-Electrodes anodized and raised above the solution. \( O_2 \) gas was passed through for 15 hrs. Then a new solution was put in the cell and the electrodes were lowered in this solution. Electrode E \( \epsilon_H = 1.22 \) V, electrode G \( \epsilon_H = 1.24 \) V. The electrodes were then raised above the solution, \( O_2 \) was passed through for 15 hrs, but no pre-electrolysis was carried out. After immersing, the potentials were: electrode E \( \epsilon_H = 1.18 \) V, electrode G \( \epsilon_H = 1.14 \) V. Now only electrode E was anodized, and both electrodes were raised above the solution. \( O_2 \) was passed through and again no pre-electrolysis was carried out. Thereafter the potentials were: electrode E \( \epsilon_H = 1.24 \) V, electrode G \( \epsilon_H = 1.02 \) V.

d-Electrodes anodized and raised above the solution. Pre-electrolysis 20 hrs, \( O_2 \) gas was passed through. The observed potentials are electrode E \( \epsilon_H = 1.24 \) V, electrode F \( \epsilon_H = 1.26 \) V, electrode G \( \epsilon_H = 1.26 \) V. All three electrodes were now shortly cathodized until the potential was 1.00 V. Thereafter they were raised above the electrolyte. Pre-electrolysis for 20 hrs, \( O_2 \) was passed through. Upon immersing in the solution the potential of electrode E rose from 1.14 to 1.25 V, the potential of F rose from 1.10 to 1.14 V and electrode G registered 1.27 V. These electrodes were now washed outside the cell with 2x distilled water, and subsequently with conc. \( HNO_3 \); \( H_2SO_4 \) and again with water. A new solution was put in the cell, pre-electrolyzed for 15 hrs, \( O_2 \) was passed through, while the electrodes were kept above the solution. Upon immersing in the electrolyte the following behaviour was observed:

Electrode E potential rose from 1.15 to 1.22 V in 4 hrs
Electrode F potential rose from 1.12 to 1.235 V in 1\( \frac{1}{2} \) hrs
Electrode G potential rose from 1.17 to 1.225 V in 1\( \frac{1}{2} \) hrs.

e-Electrode E was oxidized and raised above the solution, electrode G was cathodically reduced to 0 V and raised above the solution. Pre-electrolysis for 20 hrs, \( O_2 \) was passed through. Thereafter the potentials were: electrode E \( \epsilon_H = 1.22 \) V, electrode G \( \epsilon_H = 1.10 \) V.

Electrode E was now cathodically reduced to 0 V, and electrode G was anodized. Both electrodes raised above the solution, pre-electrolysis 20 hrs, \( O_2 \) passed through.
After immersing in the electrolyte: Electrode E $\epsilon_H = 1.03$ V, electrode G $\epsilon_H = 1.22$ V.

4.5. Conclusion

The reversible potential of the reaction

$$2 H_2O \leftrightarrow O_2 + 4 H^+ + 4e$$

can thus be obtained on platinum in 0.25 M H$_2$SO$_4$ as well as in 0.1 M NaOH. Necessary conditions are:

a. Pt must be anodized and exposed to O$_2$-gas for at least 15 hrs;
b. electrolyte must be carefully purified.

Anodization is indeed required, as is shown by experiment (e). It appears that when a completely reduced electrode is exposed to O$_2$-gas only, the potential of reaction (1) is not observed. We notice however that the potential returns to a value in the potential region where Pt is covered with oxygen. Since no external current was applied, this oxidation is evoked by reduction of O$_2$ on the Pt surface. Due to these thus formed local elements on the electrode surface the observed potential is a "mixed" potential. We have seen in the preceding chapter that the build-up of the oxygen film follows a "TEMKIN" behaviour, and that increase of coverage proceeds slower with time. Moreover we know that if the electrode is potentiostatically anodized, the surface coverage is less than a monolayer in the potential region 0.9 - 1.3 V. We may thus expect that also at the open circuit potentials $\epsilon_H = 1.10$ V and $\epsilon_H = 1.03$ V, that are observed after exposure to O$_2$-gas for 20 hrs, the surface coverage amounts to less than a monolayer.

When however the electrode is anodized, more than a monolayer will be formed and this process appears to be diffusion controlled. This process continues during the prolonged exposure to O$_2$-gas after anodization. This follows from the experiments (a) and (b); if the electrode was kept in O$_2$-gas after anodization $\epsilon_H = 1.23$ V was observed, but if the electrode was kept in N$_2$ atmosphere $\epsilon_H = 1.10$ V - 1.15 V was found.

This potential of 1.10 - 1.15 V is also often observed directly after anodization. Then again the anodic layer has not yet reached its equilibrium value, so that a mixed potential due to surface oxidation and O$_2$ reduction is established.

These potentials are of course somewhat higher than in the case of a reduced electrode since during anodization already some
oxygen had been deposited. For the \( \text{O}_2 \) reduction process we have the Tafel-relation

\[
\epsilon - \epsilon_{\text{rev}} = \frac{RT}{nF} \ln \frac{J}{J_0}
\]

At the mixed potential value 1.1 V, we can calculate from this equation, taking \( J_0 = 10^{-10} \text{ A/cm}^2 \), \( J = 10^{-9} \text{ A/cm}^2 \).

For the oxidation process we have

\[
J = J_0 \exp \left(-\gamma \phi + \frac{nF}{RT} \eta \right)
\]

(Chapter III, with \( \eta = \epsilon - \epsilon_{\text{rev}} \)).

We can say therefore that \( J_0(\text{oxidation}) < 10^{-9} \text{ A/cm}^2 \).

For high \( \theta \) values the diffusion reaction will become rate determining instead of this "TEMKIN" relation. Because indeed conditions are reached so that reaction (1) is potential determining this implies that under these conditions \( J_{\text{diff}} < 10^{-10} \text{ A/cm}^2 \).

Concluding we see that \( \epsilon_H = 1.23 \text{ V} \), corresponding with reaction (1), will only be observed if the platinum is covered with an oxygen film. During its formation this layer will be both electronic and ionic conducting. When the oxidation process has slowed down to a current density below \( 10^{-10} \text{ A/cm}^2 \), reaction (1) is potential-determining. The Pt-electrode reacts now to a redox system and this implies that its ionic conductance has been reduced. The film is then mainly electronic conducting.

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CHAPTER V

OPTICS

The preceding chapters dealt with the formation and determination of the oxygen coverage on platinum. Whether this oxygen-film is an adsorbed layer or an oxide layer cannot be established definitely by these electrochemical methods. In order to obtain more insight in this question the oxygen-layer on platinum was detected and analyzed in situ by an optical method. In this chapter the theory of optics, necessary for an understanding of the optical measurements will be given.

5.1. The laws of electromagnetism

First we will consider the case that the medium is homogeneous, isotropic, non-conducting ($\sigma = 0$) and that the field contains no electric charge density ($\rho = 0$). (5-1,2,3). The laws of electromagnetism then simplify to

\begin{align*}
\nabla^2 \mathbf{E} - \frac{\varepsilon \mu}{\varepsilon_0^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} &= 0 \\
\nabla^2 \mathbf{H} - \frac{\varepsilon \mu}{\varepsilon_0^2} \frac{\partial^2 \mathbf{H}}{\partial t^2} &= 0
\end{align*}

In this medium the electromagnetic wave is propagated with a velocity

$$v = \frac{\varepsilon_0}{\sqrt{\varepsilon \mu}}$$

in which $\mathbf{E}$ = electric vector

$\mathbf{H}$ = magnetic vector

$\varepsilon_0$ = velocity of light in vacuum

$\varepsilon$ = dielectric constant

$\mu$ = magnetic permeability

$\sigma$ = specific conductivity
According to MAXWELL, a light wave is regarded as a harmonic electromagnetic plane wave. If the electromagnetic field is monochromatic and of angular velocity $\omega$, then it follows from eq. (1) that the electric force at any time and in any point in space is represented by the equation

\[ E = A \exp i\omega t \]

with $A$ = amplitude of electric force

\[ t_i = t - \frac{\gamma_x^1 x + \gamma_y^1 y + \gamma_z^1 z}{v_1} \]

$\gamma_1$ = velocity of light in medium 1

$\gamma_x^1, \gamma_y^1, \gamma_z^1$ = direction cosines of the normal to the wave front.

5.2. Reflection and refraction in non-absorbing media

When the light wave falls on a plane boundary (XOY plane, see fig. 5-1), between two homogeneous media 1 and 2, of different optical densities, we can write:

\[
\begin{align*}
\gamma_x^i &= \sin \phi_i \\
\gamma_y^i &= 0 \\
\gamma_z^i &= \cos \phi_i \\
\phi_i &= \text{angle of incidence, i.e. angle between direction of propagation of incident wave and the normal OZ to the boundary.}
\end{align*}
\]

Fig. 5-1 Reflection and refraction of a light wave at a plane boundary.

Plane of incidence XOZ plane. Boundary plane XOY plane.
At the boundary, the incident light is partly reflected into the first medium, and partly transmitted into the second medium. This is expressed by

\[
E_i = A e^{i \omega t_i} \\
E_r = R e^{i \omega t_r} \\
E_t = T e^{i \omega t_t}
\]

The subscripts \( i \), \( r \) and \( t \) stand for incident, reflected and transmitted. \( R \) = amplitude of reflected light, \( T \) = amplitude of transmitted light,

\[
R = \frac{\gamma_x r_x + \gamma_y r_y + \gamma_z r_z}{v_1} \\
T = \frac{\gamma_x t_x + \gamma_y t_y + \gamma_z t_z}{v_2}
\]

Calling \( \phi_r \) = angle of reflection, i.e. angle between normal to wave front of reflected wave and normal to the boundary,

\( \phi_t \) = angle of transmission, i.e. angle between normal to wave front of transmitted wave and normal to the boundary,

then we have

\[
\gamma_x r = \sin \phi_r \\
\gamma_y r = 0 \\
\gamma_z r = \cos \phi_r \\
\gamma_x t = \sin \phi_t \\
\gamma_y t = 0 \\
\gamma_z t = \cos \phi_t
\]

The laws of reflection and refraction are immediately derived from these relations:

\[\sin \phi_i = \sin \phi_r \quad \text{(law of reflection)}\]

or

\[\phi_i = \pi - \phi_r\]

Since \( v = \frac{v_0}{\sqrt{\epsilon \mu}} \) and

\[n = \frac{v_0}{v} = \text{refractive index for refraction of light from vacuum into a medium.}\]

\[n = \sqrt{\epsilon \mu} \quad \epsilon = \text{frequency dependent}\]
So it follows:

(6) \[
\frac{\sin \phi_i}{\sin \phi_t} = \frac{n_2}{n_1}
\]

(Law of refraction)

The \( E \) vector is now resolved into its components parallel // and perpendicular \( \perp \) to the plane of incidence, XOZ plane (see fig. 5-1). This gives \( E_x^i, y, z \), as a function of \( A_{//} \) or \( A_{\perp} \) and of \( \phi_i \); \( E_x^r, y, z \) as a function of \( R_{//} \) or \( R_{\perp} \) and of \( \phi_t \); \( E_x^t, y, z \) as a function of \( T_{//} \) or \( T_{\perp} \) and of \( \phi_t \).

From this, equations can be derived (see 5-1,2) expressing the behaviour of // respectively \( \perp \) light upon reflection and refraction. This yields the amplitude \( T_{//} \) resp. \( T_{\perp} \) with respect to \( A_{//} \) resp. \( A_{\perp} \) and \( R_{//} \) resp. \( R_{\perp} \) with respect to \( A_{//} \) resp. \( A_{\perp} \).

(7a) \[
T_{//} = \frac{T_{//}}{A_{//}} = \frac{2 n_1 \cos \phi_i}{n_2 \cos \phi_i + n_1 \cos \phi_t} = \frac{2 \sin \phi_t \cos \phi_i}{\sin(\phi_i + \phi_t) \cos(\phi_i - \phi_t)}
\]

(7b) \[
T_{\perp} = \frac{T_{\perp}}{A_{\perp}} = \frac{2 n_1 \cos \phi_i}{n_1 \cos \phi_i + n_2 \cos \phi_t} = \frac{2 \sin \phi_t \cos \phi_i}{\sin(\phi_i + \phi_t)}
\]

(8a) \[
r_{//} = \frac{R_{//}}{A_{//}} = \frac{n_2 \cos \phi_i - n_1 \cos \phi_t}{n_2 \cos \phi_i + n_1 \cos \phi_t} = \frac{\tan(\phi_i - \phi_t)}{\tan(\phi_i + \phi_t)}
\]

(8b) \[
r_{\perp} = \frac{R_{\perp}}{A_{\perp}} = \frac{n_1 \cos \phi_i - n_2 \cos \phi_t}{n_1 \cos \phi_i + n_2 \cos \phi_t} = \frac{\sin(\phi_i - \phi_t)}{\sin(\phi_i + \phi_t)}
\]

The proportionality factors \( T_{//}, r_{//}, T_{\perp}, r_{\perp} \) are called the Fresnel coefficients.

For \( \phi_i \) and \( \phi_t \) real, these coefficients are also real.

The conditions for \( \phi_t \) real, follow from:

\[
\frac{\sin \phi_i}{\sin \phi_t} = \frac{n_2}{n_1}
\]

For \( \frac{n_2}{n_1} > 1 \), \( \sin \phi_t < \sin \phi_i \) and with \( \phi_i \) real, \( \phi_t \) is also real.

For \( \frac{n_2}{n_1} < 1 \), i.e. the second medium is less dense than the first medium, \( \sin \phi_t > \sin \phi_i \), and a real value of \( \phi_t \) is then obtained only for \( \sin \phi_i < \frac{n_2}{n_1} \).

For values of \( \sin \phi_i > \frac{n_2}{n_1} \), all the light is reflected.
5.3. Reflection at a metal surface

In the foregoing derivation, it was implied that the two media are non-conducting. Now we will consider the case that a light wave is propagated in a conducting medium ($\sigma \neq 0$). In that case, the wave equation is

\[ v^2 \frac{\hat{E}}{v_0^2} - \frac{\varepsilon}{\varepsilon_0} \frac{\partial^2 \hat{E}}{\partial t^2} + \frac{4\pi\varepsilon_0\sigma}{v_0^2} \frac{\partial \hat{E}}{\partial t} = 0 \]  

This equation implies that the wave is attenuated when propagating through that medium. Substitution of the wave equation

\[ E = A e^{i \omega t} \]

gives:

\[ v^2 \frac{\hat{E}}{v_0^2} + \frac{\varepsilon}{\varepsilon_0} \frac{\partial^2 \hat{E}}{\partial t^2} (\varepsilon - \frac{4\pi\varepsilon_0\sigma}{\omega}) = 0 \]

or with

\[ \varepsilon - \frac{4\pi\sigma}{\omega} \mu = \tilde{\varepsilon} \quad (\sim \text{denotes complex quantity}) \]

\[ (5b) \quad v^2 \frac{\hat{E}}{v_0^2} - \frac{\tilde{\varepsilon}}{\varepsilon_0} \frac{\partial^2 \hat{E}}{\partial t^2} = 0 \]

Comparison with eq (5) shows that $\varepsilon$ has been substituted by the complex quantity $\tilde{\varepsilon}$.

Likewise Maxwell's relation $n = \sqrt{\varepsilon \mu}$ is now written as

\[ \tilde{n} = n \ (1 - iK) \]

$K$ = absorption index.

The relation between $n$, $K$ and the material constants $\varepsilon, \sigma, \mu$ is given by:

\[ (10) \quad n^2 (1 - K^2) = \mu \varepsilon \]

\[ (11) \quad n^2 K = \frac{2\pi\sigma\mu}{\omega} \]

It should be realized that both $\varepsilon$ and $\sigma$ are frequency-dependent.

HEAVENS (5-3) has pointed out that several notations for the complex quantity $\tilde{n}$ are used e.g.:

\[ \tilde{n} = n - iK \]
\[ \tilde{n} = n \ (1 - iK) \]
\[ \tilde{n} = n \ (1 + iK) \]
but it appears that there is "no logical preference for the one above the other". Here the notation $n = n(1 - iK)$ is used.

In the following part we will deal with light that is incident from a non-conducting medium ($n_1$) on a conducting medium ($n_2$). A metal is taken as the second medium. The law of refraction is then:

$$\frac{\sin \phi_i}{\sin \phi_t} = \frac{n_2}{n_1}$$

It follows that $\phi_t$ is now also a complex quantity.

With respect to the light reflected at this metal surface, we make use of eq. (8a, b):

$$R_{//} = r_{//} A_{//}$$
$$R_{\perp} = r_{\perp} A_{\perp}$$

The Fresnel coefficients $r_{//}$ and $r_{\perp}$ are a function of $\phi_i$ and $\phi_t$ and are now likewise complex. This is expressed by

$$r_{//} = \rho_{//} e^{i\delta_{//}}$$
$$r_{\perp} = \rho_{\perp} e^{i\delta_{\perp}}$$

$$\rho_{//}, \rho_{\perp} = \text{absolute value of reflection-coefficient}$$
$$\delta_{//}, \delta_{\perp} = \text{phase change.}$$

While the phase of a reflected component at a non-conducting surface is equal to the phase of the corresponding component of the incident wave or differs from it by $\pi$, in the case of reflection at a conducting surface the two components undergo different phase-jumps, since $\delta_{//}$ and $\delta_{\perp}$ are different functions of $\phi_t$ and $\phi_i$. This implies that, if the incident light is linearly polarized, the reflected light is in general elliptically polarized (fig. 5-2). With $\alpha = \text{angle between plane of vibration and the normal to the plane of incidence}$, we have

$$\tan \alpha_i = \frac{A_{//}}{A_{\perp}}$$
$$\tan \alpha_x = \frac{R_{//}}{R_{\perp}}$$

Substitution of eq (8a) and (8b) gives:

$$\tan \alpha_x = \frac{R_{//}}{R_{\perp}} = -\frac{\cos (\phi_i + \phi_t)}{\cos (\phi_i - \phi_t)} \tan \alpha_i$$ (12)
Fig. 5-2 Direction of vibration of incident linearly polarized light is turned upon reflection. At a non-conducting surface, the reflected light is still linearly polarized; at a conducting surface the reflected light is in general elliptically polarized.

This relation clearly shows that on reflection the plane of vibration is always turned, the magnitude depends on $\theta_i$ and $\theta_t$ or on $\phi_i$ and the refractive indices.

For $\theta_t$ is complex, eq. (12) can be written:

$$\tan \alpha_r = \frac{R/}{R_\perp} = \frac{\rho/}{\rho_\perp} e^{i(\delta/ - \delta_\perp)} \frac{A/}{A_\perp}$$

$$\tan \alpha_r = \frac{\rho/}{\rho_\perp} e^{i\Delta} \tan \alpha_i$$

$$\Delta = \delta/ - \delta_\perp$$

For $\Delta = 0$  $\tan \alpha_r = \frac{\rho/}{\rho_\perp} \tan \alpha_i$
\( \frac{\rho//}{\rho_\perp} \) is more useful written as \( \tan \psi \). *)

The ratio of the amplitudes of the reflected light // and \( \perp \) to the plane of incidence is now

\[
\frac{R//}{R_\perp} = \tan \psi \ e^{i\Delta} \tan \alpha_i
\]

\( \psi \) and \( \Delta \) characterize the reflected polarized light. The measurements of these two quantities is performed by introducing a known phase-difference between \( R// \) and \( R_\perp \) so that the total phase difference becomes zero. Then \( \tan \alpha_r = \tan \psi \tan \alpha_i \).

The light is then again linearly polarized and \( \alpha_r \) can be determined. From eq (12) and eq (13) it follows:

\[
\tan \psi \ e^{i\Delta} = -\frac{\cos (\phi_i + \phi_t)}{\cos (\phi_i - \phi_t)}
\]

Further we have:

\[
\frac{\sin \phi_i}{\sin \phi_t} = \frac{n_2}{n_1}
\]

(Suffix 1 refers to the first medium (transparent), suffix 2 to the second medium, the absorbing metal surface). \( \Delta \) and \( \psi \) are thus related to the optical constants \( n_2 \) and \( K_2 \) of the metal. This was pointed out for the first time by DRUDE (5-5) and by TRONSTAD (5-4).

They calculated, taking air as the first medium (\( n_1 = 1 \))

\[
\frac{\sqrt{n_2^2 - \sin^2 \phi_i}}{\sin \phi_i \tan \phi_i} = \frac{\cos 2\psi - i \sin 2\psi \sin \Delta}{1 + \sin 2\psi \cos \Delta}
\]

*) Born & Wolf (5-1), and Mayer (5-2) define \( \psi \) as \( \tan \psi = \frac{\rho_\perp}{\rho//} \)

Tronstad (5-4) and others define \( \psi \) as \( \tan \psi = \frac{\rho//}{\rho_\perp} \)

The latter definition is used here throughout.

Accordingly \( \alpha_i \) and \( \alpha_r \) are defined as

\[
\tan \alpha_i = \frac{A//}{A_\perp} \quad \text{and} \quad \tan \alpha_r = \frac{R//}{R_\perp}
\]
Neglect of \( \sin^2 \psi_i \) with respect to \( n_2^2 \) yields:

\[
(16a) \quad n_2 = \frac{\sin \psi_i \tan \psi_i \cos 2\psi}{1 + \sin 2\psi \cos \Delta}
\]

\[
(16b) \quad K_2 = \tan 2\psi \sin \Delta
\]

According to TRONSTAD, these equations are to be multiplied by \( n_1 \) when the first medium has a refractive index \( n_1 \neq 1 \).

Without neglect of \( \sin^2 \psi_i \), eq. (11) gives \( n_2 \) and \( K_2 \) in the combination \( 2n_2^2 K_2 \) and \( n_2^2 (1-K_2^2) \). (5-1)

\[
(17a) \quad n_2^2 (1-K_2^2) = n_1^2 \sin^2 \psi_i \left( 1 + \frac{\tan^2 \psi_i (\cos^2 2\psi - \sin^2 2\psi \sin^2 \Delta)}{(1 + \sin 2\psi \cos \Delta)^2} \right)
\]

\[
(17b) \quad 2n_2^2 K_2 = \frac{n_1^2 \sin^2 \psi_i \tan^2 \psi_i \sin 4\psi \sin \Delta}{(1 + \sin 2\psi \cos \Delta)^2}
\]

The value of \( \Delta \).

The relative phase difference \( \Delta \) depends on the angle of incidence \( \psi \) and on \( n_2 \).

For \( \psi = 0 \) \quad \tan \psi e^{i\Delta} = -1 \quad \text{thus} \quad \Delta = \pi
\]

\[
\tan \psi = 1 \quad \tan \alpha_R = -\tan \alpha_i
\]

For \( \psi = \pi/2 \) \quad \tan \psi e^{-i\Delta} = +1 \quad \text{thus} \quad \Delta = 0
\]

\[
\tan \psi = 1 \quad \tan \alpha_R = +\tan \alpha_i
\]

There will thus exist an angle \( \bar{\psi}_i \) (= principle angle of incidence) for which \( \Delta = \pi/2 \).

DRUDE's experiments on platinum have shown that \( \bar{\psi}_i = 78^\circ30' \) for platinum. For an angle of incidence around \( 70^\circ \), \( \Delta \) is thus larger than \( \pi/2 \) so that for reflection at platinum

\[
\pi/2 < \Delta < \pi
\]

5.4. The presence of a non-absorbing layer on a metal surface

Let us assume now that a layer of thickness \( L \) is present on the metal surface. It is assumed that the layer is homogeneous, and that its refractive index does not vary with thickness. We will first consider a non-absorbing layer with refractive index \( n_1 \).
Fig. 5-3 shows the change in amplitude $A$ of a light beam $E = A e^{i\omega t}$ upon reflection and refraction at the two boundaries I and II. Using the Fresnel - reflection and refraction coefficients (eq. 7a,b and 8a,b), one can easily follow the change in amplitude $A$ of a light beam $E = A \exp(i\omega t)$ upon reflection and refraction at two boundaries I and II.

**Fig. 5-3** Reflection and refraction of a plane wave incident on a metal surface covered with a layer of thickness $L$.

I: boundary between medium 0 (refractive index $n_0$) and layer of thickness $L$ (refractive index $n_1$)

II: boundary between layer of thickness $L$ and the metal (refractive index $n_2$).

Medium 0 and 1 are non-absorbing.

In this figure $t_S$ corresponds with propagation from medium 0 into 1, and $t_S'$ with propagation from medium 1 into 0. It follows from eq. (8a and b) that $r_S = - r_S'$ so that a change of sign has been taken into account for the reflection in the layer at boundary I.

The phase changes are determined by the thickness of the layer ($L$) and the angle of refraction $\phi_I$:

$$\Delta = \frac{2\pi}{\lambda} n_1 L \cos \phi_I$$
This phase change is for beam (1) 
\[0\]
(2) \[\frac{4\pi}{\lambda} n_1 L \cos \phi_1\]
(3) \[\frac{8\pi}{\lambda} n_1 L \cos \phi_1\]

The total amplitude of reflected waves is the sum of that for the beams (1), (2), (3) etc.

\[R = Ae^{i\omega t} \left( r_{1+} r_{II} t_{1+} e^{-\frac{4\pi i}{\lambda} n_1 L \cos \phi_1} - r_{II}^2 t_{1+} e^{-\frac{8\pi i}{\lambda} n_1 L \cos \phi_1} \right) + \]
\[r_{II}^2 t_{1+} e^{-\frac{12\pi i}{\lambda} n_1 L \cos \phi_1} \]

With \(r^2 + tt' = 1\) and neglect of higher order terms, we have

\[(18) \quad R = Ae^{i\omega t} \frac{r_{1+} r_{II} e^{-\frac{4\pi i}{\lambda} n_1 L \cos \phi_1}}{1 + r_{II} e^{-\frac{4\pi i}{\lambda} n_1 L \cos \phi_1}}\]

This relationship holds for both the // and the \(\perp\) component.

For linearly polarized light, with \(\alpha_\perp = 45^\circ\) we can write for the amplitude-ratio \(R_{//}/R_{\perp}\) of the reflected light:

\[(19) \quad R_{//} = \tan \psi_{\perp} = \frac{r_{//} + r_{II} e^{-\frac{4\pi i}{\lambda} n_1 L \cos \phi_1}}{1 + r_{II} e^{-\frac{4\pi i}{\lambda} n_1 L \cos \phi_1}} \times \frac{1 + r_{//} r_{II} e^{-\frac{4\pi i}{\lambda} n_1 L \cos \phi_1}}{1 + r_{II} e^{-\frac{4\pi i}{\lambda} n_1 L \cos \phi_1}}\]

in which the Fresnel coefficients are given by:

\[r_{I} = \frac{n_0 \cos \phi_0 - n_1 \cos \phi_1}{n_0 \cos \phi_0 + n_1 \cos \phi_1} \quad r_{//} = \frac{n_1 \cos \phi_0 - n_0 \cos \phi_1}{n_1 \cos \phi_0 + n_0 \cos \phi_1}\]
\[r_{II} = \frac{n_1 \cos \phi_1 - n_2 \cos \phi_2}{n_1 \cos \phi_1 + n_2 \cos \phi_2} \quad r_{II} = \frac{n_2 \cos \phi_1 - n_1 \cos \phi_2}{n_2 \cos \phi_1 + n_1 \cos \phi_2}\]

Since we are considering a non-absorbing layer on an absorbing surface (metal), the coefficients \(r_{I} \), \(r_{//}\) are real, and \(r_{II} \), \(r_{II} \) are complex.
DRUDE has shown, that for small values of L (L << \lambda), the ratio $R_{//}/R_{\perp}$ can be simplified to

$$
\frac{R_{//}}{R_{\perp}} = \frac{n_2 \cos \phi - n_o \cos \phi_2}{n_2 \cos \phi + n_0 \cos \phi_2} \times \frac{n_0 \cos \phi + n_2 \cos \phi_2}{n_0 \cos \phi - n_2 \cos \phi_2} \times
$$

$$
\left[ 1 + \frac{4\pi i L}{\lambda} \left( \frac{n_o \cos \phi_2 (n_1^2 \cos \phi_2 - n_2^2 + \frac{n_2^4}{n_1^2} \sin^2 \phi_2)}{(n_2^2 \cos^2 \phi_2 - n_0^2 \cos^2 \phi_2)} \right) - \frac{n_o \cos \phi_2 (n_1^2 - n_2^2)}{(n_1^2 \cos \phi - n_2 \cos \phi_2)} \right]
$$

The first 2 factors in equation (20) are equal to the ratio of the reflection coefficients in the absence of a layer, thus we have:

$$
(tan \phi e^{i\Delta})_{\text{Layer}} = (tan \phi e^{i\Delta})_{\text{Bare surface}} \times \left[ 1 + \frac{4\pi i L}{\lambda} \right] \text{etc}
$$

We shall write this as:

$$
tan \psi_L \frac{i(\Delta - \Delta_0)}{tan \psi} = tan \psi e^{i\Delta} \times \left[ 1 + \frac{4\pi i L}{\lambda} \right] \text{etc}
$$

Substituting

$$
\sin \phi_2 = \frac{n_0}{n_2} \sin \phi_0, \text{ gives:}
$$

$$
\frac{tan \psi_L}{tan \psi} e^{i(\Delta \lambda)} = 1 + \frac{4\pi i}{\lambda} \frac{n_0 \cos \phi_2}{n_1^2 (n_2^2 - n_0^2) (n_2^2 - n_0^2) \sin^2 \phi_2}
$$

In this formula $n_1$ = real, $n_2$ is complex.

By further approximation DRUDE and later TRONSTAD have derived a rather simple relationship. Writing:

$$
tan \psi_L = tan \psi (1 + \delta)
$$

$$
2 \psi_L = 2 \psi + \delta \sin 2 \psi
$$

and equating the real and imaginary parts they obtained

$$
\Delta_L = \Delta \lambda - \frac{4\pi L}{\lambda} \frac{(n_1^2 - n_0^2) n_0 \sin^2 \phi \cos \phi}{(\cos^2 \phi - a_2 n_0^2)^2 + a_2^4 n_0^4} \left[ \frac{1}{n_1^2 - a_2^2} (\cos \phi \phi - n_0 a_2^2) + a_2^2 n_0^2 \right]
$$

$$
2 \psi_L = 2 \psi + \sin 2 \psi \frac{4\pi L}{\lambda} \frac{(n_1^2 - n_0^2) n_0 \sin^2 \phi \cos \phi}{(\cos^2 \phi - a_2 n_0^2)^2 + a_2^4 n_0^4} \left[ \frac{1}{n_1^2 - a_2^2} (\cos \phi \phi - n_0 a_2^2) - (\cos^2 \phi - a_2^2 n_0^2) a_2^2 \right]
$$
in which
\[ a_2 = \frac{1-K_2}{n_2^2 (1+K_2)^2} \quad a_2' = \frac{2K_2}{n_2^2 (1+K_2)^2}. \]

For simplicity sake, the suffix 0 in \( \phi \) is omitted further on.

It may be mentioned here that in several papers and textbooks a typographical error appears, namely in eq (23) the first term within the brackets

\[ a_2' n_0^2 \left( \frac{1}{n_1^2} - a_2 \right) \]

is sometimes written as

\[ a_2' n_1^2 \left( \frac{1}{n_1^2} - a_2 \right) \]

cf Mayer (5-2), Tronstad (5-4b)

but correctly in (5-4a) and (5-4c).

The formulas given here, thus apply for light incident under angle \( \phi \) upon a metal surface \((n_2K_2)\), coated with a thin non-absorbing layer \((n_1)\) of thickness \(L\), in a transparent medium of index \(n_0\).

5.5. The presence of an absorbing layer on a metal surface

In the event of an absorbing layer \((K_1\neq0)\), the derivation leads to a more complicated formula. In equation (21) \(n_1\) is now likewise a complex quantity \(n_1 = n_1 (1 - iK_1)\).

For this case, we have derived using again \(L << \lambda\) (see appendix)

(24)

\[ \tan \psi_L e^{i\lambda L} = \tan \psi \left[ 1 + \frac{4n_1^2}{\lambda} \frac{\sin^2 \phi \cos \psi \ n_0^7}{(n_0^2 \phi + a_2' n_0^2 + a_2 a_1')^2} (P + iN) \right]. \]

\(P\) and \(N\) are given by eq. (25) and (26).

Eq. (25):

\[ P = (a_1 - a_2) \left[ (a_1^2 + a_1'^2 - a_0 a_1) \left[ a_0^2 \cos^2 \phi - a_0 a_2 + (a_2^2 - a_2') \sin^2 \phi \right] + \right. \]

\[ - a_0^2 a_1 a_2' + 2a_0 a_1 a_2 a_2' \sin^2 \phi \left] \right. \]

\[ - (a_1 - a_2') \left[ (a_1^2 + a_1'^2 - a_0 a_1) (a_0 a_2' - 2a_2 a_2' \sin^2 \phi) + \right. \]

\[ + a_0 a_1' \left[ a_0^2 \cos^2 \phi - a_0 a_2 + (a_2^2 - a_2') \sin^2 \phi \right] \left] \right]. \]
Eq. (26):

\[ N = (a_1 - a_2) \left\{ (a_1^2 + a_1' - a_0 a_1) \left( a_0 a_2 - 2a_2 a_2' \sin^2 \phi \right) + a_0 a_1' \left[ a_0^2 \cos^2 \phi - a_0 a_2 + (a_2^2 - a_2' \sin^2 \phi) \right] \right\} + \\
+ (a_1' - a_2') \left\{ (a_1^2 + a_1' - a_0 a_1) \left[ a_0^2 \cos^2 \phi - a_0 a_2 + \\
+ (a_2^2 - a_2' \sin^2 \phi) \right] - a_0^2 a_1 a_2 + 2a_0 a_1' a_2 a_2' \sin^2 \phi \right\} \]

in which

\[ a_1 = \frac{1 - K_1^2}{n_1^2 (1 + K_1^2)^2} \]
\[ a_1' = \frac{2 K_1}{n_1^2 (1 + K_1^2)^2} \]
\[ a_2 = \frac{1 - K_2^2}{n_2^2 (1 + K_2^2)^2} \]
\[ a_2' = \frac{2 K_2}{n_2^2 (1 + K_2^2)^2} \]
\[ a_0 = \frac{1}{n_0} \]

Now again

\[ \tan \psi_L = \tan \psi (1 + \delta) \]
\[ 2 \psi_L = 2 \psi + \delta \sin 2 \psi \]

gives:

\[ (27) \quad \Delta_L - \Delta = \frac{4 \pi L}{\lambda} \frac{\sin^2 \phi \cos \phi n_0^7}{\left[ (\cos^2 \phi - a_2 n_0^2)^2 + a_2'^2 n_0^4 \right]^{\frac{p}{(a_1^2 + a_1'^2)}}} \]
\[ (28) \quad 2 \psi_L - 2 \phi = -\sin 2 \psi \frac{4 \pi L}{\lambda} \frac{\sin^2 \phi \cos \phi n_0^7}{\left[ (\cos^2 \phi - a_2 n_0^2)^2 + a_2'^2 n_0^4 \right]^{\frac{N}{(a_1^2 + a_1'^2)}}} \]

These formulas were checked by substituting \( K_1 = 0 \); the Drude - Tronstad formulas (22) - (23) were then again obtained.

When the approximation \( L \ll \lambda \) is not allowed, the complete formula (19) should be used (5-2, 5-6), in which all the Fresnel coefficients are complex.
Appendix

Derivation of eq. (24)

eq. (21):

\[ \tan \psi_L e^{i \Delta L} = \tan \psi e^{i \Delta} \left[ 1 + \frac{4 \pi i}{\lambda} \cos \phi \sin^2 \phi \cdot n_0 n_2 \frac{(n_2^2 - n_1^2) (n_0^2 - n_1^2)}{n_1^2 (n_2^2 - n_0^2) [n_2^2 - (n_2^2 + n_0^2) \sin^2 \phi]} \right] \]

Substitution of

\[ a_0 = \frac{1}{n_0^2} \quad a_1' = \frac{1}{n_1^2} \quad a_2 = \frac{1}{n_2^2} \]

gives

\[ \tan \psi_L e^{i \Delta L} = \tan \psi e^{i \Delta} \left[ 1 + \frac{4 \pi i}{\lambda} \cos \phi \sin^2 \phi \cdot F(a) \right] \]

in which \( F(a) = \frac{\sqrt{a_0} (a_1 - a_2) (a_1 - a_0)}{a_1 (a_0 - a_2) \left[ a_0 - (a_0 + a_2) \sin^2 \phi \right]} \)

In the case of an absorbing layer on an absorbing surface, one can write:

\[ a_0 = a_0 \]
\[ a_1 = a_1 + i a_1' \]
\[ a_2 = a_2 + i a_2' \]

\( F(a) \) is then equal to:

\[ F(a) = \frac{\sqrt{a_0} (a_1 + i a_1' - a_0) (a_1 + i a_1' - a_2 - i a_2')}{(a_1 + i a_1') (a_0 - a_2 - i a_2') \left[ a_0 - (a_0 + a_2 + i a_2') \sin^2 \phi \right]} \]

\[ F(a) = \frac{\sqrt{a_0} (a_1 + i a_1' - a_0) (a_1 + i a_1' - a_2 - i a_2')}{(a_1 + i a_1')^2 + a_1'^2} \left[ (a_0 - a_2 - i a_2') \sin^2 \phi \right] \]

\[ F(a) = \frac{(a_0 - a_2 - i a_2')}{(a_0 - a_2 - i a_2') \left[ a_0 - (a_0 + a_2 - i a_2') \sin^2 \phi \right] + a_2'^2 \sin^2 \phi} \]

Thus \( F(a) = \frac{F_1(a)}{F_2(a)} \)

Calculation of \( F_1(a) \):

\[ F_1(a) = \sqrt{a_0} \left[ a_1^2 + a_1'^2 - a_0 (a_1 - i a_1') \right] \left[ (a_1 - a_2) + i (a_1' - a_2') \right] \times \]

\[ \left[ a_0 - a_2 + i a_2' \right] \left[ a_0 \cos^2 \phi - a_2 \sin^2 \phi + i a_2' \sin^2 \phi \right] \]
\[ F_1(a) = \sqrt{a_0} \left\{ (a_0-a_2) \left( a_1 - a_2 \right) - a_2' (a_1' - a_2') + i \left( (a_1' - a_2') (a_0-a_2) + \right. \right. \]
\[ \left. \left. + a_2' (a_1' - a_2') \right\} \left[ (a_1^2 + a_1'^2 - a_0 a_1^2) (a_0 \cos^2 \phi - a_2 \sin^2 \phi) - a_0 a_1' a_2' \sin^2 \phi + \right. \]
\[ \left. + i \left( (a_0 \cos^2 \phi - a_2 \sin^2 \phi) a_0 a_1' + a_2' \sin^2 \phi (a_1^2 + a_1'^2 - a_0 a_1^2) \right) \right] \]

Put \( B = a_1^2 + a_1'^2 - a_0 a_1 \)

\[ F_1(a) = \sqrt{a_0} (a_1 - a_2) \left[ (a_0-a_2)B(a_0 \cos^2 \phi - a_2 \sin^2 \phi) - a_0 a_1' a_2' \sin^2 \phi (a_0-a_2) + \right. \]
\[ \left. - (a_0 \cos^2 \phi - a_2 \sin^2 \phi) a_0 a_1' a_2' - a_2'^2 \sin^2 \phi \quad B \right] + \]
\[ + \sqrt{a_0} (a_1' - a_2') \left[ -a_2' B(a_0 \cos^2 \phi - a_2 \sin^2 \phi) + a_2'^2 a_0 a_1' \sin^2 \phi + \right. \]
\[ \left. - (a_0-a_2) (a_0 \cos^2 \phi - a_2 \sin^2 \phi)(a_0 a_1')-(a_0 a_2) a_2' \sin^2 \phi B \right] + \]
\[ \sqrt{a_0} i (a_1' - a_2') \left[ a_2' B(a_0 \cos^2 \phi - a_2 \sin^2 \phi) - a_0 a_1' a_2'^2 \sin^2 \phi + \right. \]
\[ \left. + (a_0-a_2) (a_0 \cos^2 \phi - a_2 \sin^2 \phi) a_0 a_1' + (a_0-a_2) a_2' \sin^2 \phi B \right] + \]
\[ + \sqrt{a_0} i(a_1' - a_2') \left[ (a_0-a_2)B(a_0 \cos^2 \phi - a_2 \sin^2 \phi)-(a_0-a_2)a_0 a_1' a_2'^2 \sin^2 \phi + \right. \]
\[ \left. - a_2' a_0 a_1' (a_0 \cos^2 \phi - a_2 \sin^2 \phi)-a_2'^2 \sin^2 \phi B \right] \]

\[ F_1(a) = \sqrt{a_0} (a_1 - a_2) \left[ B(a_0 \cos^2 \phi a_0 a_2 + a_2' \sin^2 \phi - a_2' \sin^2 \phi) - a_0 a_1' a_2'^2 \sin^2 \phi + \right. \]
\[ + 2a_0 a_1' a_2' a_2'^2 \sin^2 \phi \right] \left[ -\sqrt{a_0} (a_1' - a_2') \left[ B(a_0 a_2' - 2a_2 a_2' \sin^2 \phi) - a_2'^2 a_0 a_1' \sin^2 \phi + \right. \right. \]
\[ \left. \left. + a_0 a_1' \cos^2 \phi - a_0 a_2' a_2 + a_0 a_1' a_2'^2 \sin^2 \phi \right] + \right. \]
\[ + i \sqrt{a_0} (a_1' - a_2') \left[ B(a_0 a_2' - 2a_2 a_2' \sin^2 \phi) - a_2'^2 a_0 a_1' \sin^2 \phi + \right. \]
\[ \left. + a_0 a_1' \cos^2 \phi - a_0 a_2' a_2 + a_2'^2 a_0 a_1' \sin^2 \phi \right] + \right. \]
\[ + i \sqrt{a_0} (a_1' - a_2') \left[ B(a_0 a_2' \cos^2 \phi + a_2' \sin^2 \phi-a_0 a_2' - a_2'^2 \sin^2 \phi + \right. \]
\[ \left. - a_0 a_1' a_2' + 2 a_0 a_1' a_2' a_2 \sin^2 \phi \right] \]
Now we put
\[ P = (a_1 - a_2) \left( B(a_0^2 \cos^2 \phi - a_0 a_2 + a_2^2 \sin^2 \phi) - a_0^2 a_1^2 + a_2 + 2a_0 a_1 \right) \sin^2 \phi - \left( a_1 - a_2 \right) \left( B(a_0 a_2 - 2a_2 a_1 \sin^2 \phi) - a_2^2 a_1^2 \sin^2 \phi + a_0^2 a_1^2 \right) \]

\[ N = (a_1 - a_2) \left( B(a_0 a_2 - 2a_2 a_1 \sin^2 \phi) - a_2^2 a_1^2 \sin^2 \phi + a_0^2 a_1^2 \cos^2 \phi - a_0 a_2^2 a_1^2 \sin^2 \phi \right) + (a_1 - a_2) \left( B(a_0 a_2 \cos^2 \phi + a_2^2 \sin^2 \phi) + a_0^2 a_1^2 \right) \]

\[ F_1(a) = \sqrt{a_0} (P + i N) \]

Calculation of \( F_2(a) \)

\[ F_2(a) = (a_1^2 + a_1^2)^2 \left( \left( a_0 - a_2 \right)^2 + a_2^2 \right)^2 \left( a_0^2 - (a_0 + a_2) \sin^2 \phi \right)^2 + a_2^2 \sin^2 \phi \]

Since \( a_2 \) and \( a_1^2 \) are small with respect to 1, one may write (ref.5-5).

\[ F_2(a) = (a_1^2 + a_1^2) \left( a_0^2 + a_2^2 + a_1^2 \right)^2 \left( a_0 \cos^2 \phi + a_2^2 \sin^2 \phi \right)^2 + a_2^2 \sin^2 \phi \]

\[ F(a) = \frac{\sqrt{a_0} (P + i N)}{(a_1^2 + a_1^2) a_0^2 \left( a_0 \cos^2 \phi - a_2 \right)^2 + a_2^2 \sin^2 \phi} \]

With \( a_0 = \frac{1}{n_0^2} \), we get

\[ F(a) = \frac{n_0^7 (P + i N)}{(a_1^2 + a_1^2) \left( \cos^2 \phi - a_2 n_0^2 \right)^2 + a_2^2 n_0^2} \]

Thus:

\[ \tan L e^{i \Lambda} = \tan e^{i \Lambda} \left[ 1 + \frac{4 \frac{i}{\lambda} - L}{\cos \phi \sin^2 \phi n_0^7 \left( \left( \cos^2 \phi - a_2 n_0^2 \right)^2 + a_2^2 n_0^2 \right)} \frac{(P + i N)}{(a_1^2 + a_1^2)} \right] \]
<table>
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<th>Reference</th>
<th>Author(s)</th>
<th>Publication Details</th>
</tr>
</thead>
</table>
| 5-4       | L. Tronstad | a. Trans. Faraday Soc. 31 (1935) 1151 
             |           | b. Trans. Faraday Soc. 29 (1933) 502 
             |           | c. K. Norske vid Skrifter Trondhjem 1931 no.1 1-248. |
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CHAPTER VI

THE ELLIPSOMETER

After having dealt with the theory of reflection of light at a metal surface, we shall now go into the practical question how $\Delta$ and $\psi$ are measured.

The phase retardation $\Delta$ and the relative change in amplitude-ratio $\psi$ of the $//\text{ and } \perp$ components of the reflected light can be observed with an ellipsometer. This instrument measures the state of polarization of light. The name "ellipsometer" was coined by A. Rothen in 1944.

6.1. Theory

The reflection of a lightbeam at a plane boundary is pictured in fig. 6-1a. The incident light is linearly polarized, thus the plane of vibration makes an angle $\alpha_\perp$ with the normal to the plane of incidence. After reflection, the orientation of the vibration is changed ($\alpha_\parallel$) and a phase difference $\Delta$ between the two components of the light $//\text{ and } \perp$ to the plane of incidence, has been...
introduced. This means that the reflected light is elliptically polarized. The axes of the ellips being a and b, the ellipticity \( \chi \) is defined by

\[
\tan \chi = \frac{b}{a}
\]

\( a \) = major axis
\( b \) = minor axis

This ellips is oriented with its major and minor axis \( \perp \) and // to the plane of incidence only in the case that \( \Delta = \pi/2 \); the axes of the ellips are then equal to the amplitudines \( OA \) and \( OB \) of the components of the electrical vector \( \perp \) and // to the plane of incidence. (fig. 6-1b). For \( \Delta \) values \( \neq 0, \neq \pi/2 \) the major axis of the ellips is tilted with respect to the normal to the plane of incidence.

At a metal surface \( \Delta \) is always \( > \pi/2 \). The \( \perp \) and // component undergo different phase jumps (\( \delta \perp \) and \( \delta // \)) upon reflection and it can

![Fig. 6-1b](image-url)
be shown (6-1) that \( \delta_\| > \delta_\perp \) i.e. the \( \| \) component is in advance of the \( \perp \) component. Therefore it follows that if the incident vibration is in the first or third quadrant (fig. 6-1b) the ellips characterizing the reflected light is dextrorotary and the major axis is rotated clockwise with respect to the normal to the plane of incidence.

The angle between major axis and normal to the plane of incidence is called \( \phi \); hence the reflected light is defined by \( \chi \) and \( \phi \).

6.2. Instrumental

These 2 quantities \( \chi \) and \( \phi \) are measured with the ellipsometer (6-2). The set up of the instrument is given in fig. 6-2. The "thin film ellipsometer" is manufactured by O.C. RUDOLPH & SONS, CALDWELL N.J. type 437-200E. This instrument as used in our experiments has a horizontal sample-carrier.

![Fig. 6-2 Block diagram of the ellipsometer.](image)

The light source is a mercury arc with a filter for the 5461 Å line. After passing the polarizer, the light is linearly polarized. For all measurements \( \alpha_\perp \) is set at 45°. In the reflected beam a quarter wave plate is inserted which is placed thus that the phase difference \( \Delta \) is compensated. The resulting linear polarized light is subsequently extinguished by means of the ana-
lyzer. There are of course two compensating positions for the $\lambda/4$ plate, see fig. 6-3:

1. **Fast** axis of the $\lambda/4$ plate coincides with major axis:
   Since the $\parallel$ component is in advance of the $\perp$ component this implies that the original phase difference is reduced to zero.

2. **Slow** axis of the $\lambda/4$ plate coincides with major axis:
   this gives an increase of the retardation of the $\perp$ component

---

Fig. 6-3 By insertion of a quarterwave plate the elliptically polarized light becomes linearly polarized.

with respect to the $\parallel$ component. The phase difference is now $\pi$
$\psi$ is found from the position of the $\lambda/4$ plate;
$\chi$ is found as either the sum or the difference of the positions of $\lambda/4$ plate and analyzer.

The measured values $\chi$ and $\psi$ must then be transformed to $\psi$ and $\Delta$ because we are interested in the ratio $R_{//}$ and not in the ratio $\frac{b}{a}$ (axes of the ellips).
The formulas are:
\[ \tan (x - \Delta) = \frac{\tan 2\chi}{\sin 2\beta} \]
\[ \cos 2\alpha_r = \cos 2\chi \cos 2\beta \]
The derivation is given in the appendix.
The relation between \( \alpha_r \) and \( \psi \) is given by
\[ \tan \alpha_r = \tan \psi \tan \alpha_i \]

6.3. Cell

The object of the experiments was to measure on platinum the coverage with oxygen during anodization in an electrolytic solution. Platinum foil serves as the bottom of the cell, cemented to the cell with araldite. We have used a cell in which the light enters and leaves the cell through windows, placed perpendicular to the light beam.

By this arrangement the direction of vibration (defined by \( \alpha_i \)) does not change when the light enters the cell. Likewise there is no change in \( \alpha_r \) when the light leaves the cell. So for our experiments:
\[ \tan \psi = \frac{\tan \alpha_r}{\tan \alpha_i} \]
\( \alpha_i \) is set at \( 45^\circ \), thus \( \psi = \alpha_r \).

Appendix

Derivation of the transformation formulas:
The elliptical vibration \( m = a \cos t \)
\[ n = b \sin t \quad \text{with} \quad \tan \chi = \frac{b}{a} \]
is to be described with the set of axes \( x \) and \( y \) (fig. 6-4). The
axes are rotated over angle $\delta$ with respect to m, n. (6-3).
In the x-y system, the vibration is described by
\[ x = p \cos (t + \delta_1) \]
\[ y = q \cos (t + \delta_2). \]

Transformation gives:
\[ x = m \cos \delta - n \sin \delta \]
\[ y = n \cos \delta + m \sin \delta \]

Equating:
\[ p \cos (t + \delta_1) = a \cos t \cos \delta - b \sin t \sin \delta \]
\[ q \cos (t + \delta_2) = b \sin t \cos \delta + a \cos t \sin \delta \]
\[ p \cos \delta_1 = a \cos \delta \]
\[ q \cos \delta_2 = a \sin \delta \]
\[ p \sin \delta_1 = b \sin \delta \]
\[ -q \sin \delta_2 = b \sin \delta \]

(1)
\[ p^2 + q^2 = a^2 + b^2 \]
(2)
\[ p^2 - q^2 = (a^2 - b^2) (\cos^2 \delta - \sin^2 \delta) \]
(3)
\[ pq \sin (\delta_1 - \delta_2) = ab (\cos^2 \delta + \sin^2 \delta) \]
\[ pq \sin (\delta_1 - \delta_2) = ab \]
(4)
\[ pq \cos (\delta_1 - \delta_2) = (a^2 - b^2) \sin \delta \cos \delta \]
\[ 2 pq \cos (\delta_1 - \delta_2) = (a^2 - b^2) \sin 2\delta \]

(3) divided by (4) gives
\[ \tan (\delta_1 - \delta_2) = \frac{2 ab}{(a^2-b^2) \sin 2\delta} \]
\[ \tan \chi = \frac{b}{a} \]

So
\[ \sin 2\chi = \frac{2 ab}{a^2 + b^2} \]
\[ \cos 2\chi = \frac{a^2-b^2}{a^2+b^2} \]
\[ \tan 2\chi = \frac{2 ab}{a^2-b^2} \]

(5)
\[ \frac{2 pq \sin (\delta_1 - \delta_2)}{p^2 + q^2} = \frac{2 ab}{a^2+b^2} \]

Further: (3) divided by (1) gives:
By definition: \( \tan \alpha_r = \frac{q}{p} \) so that

\[
(6) \quad \sin 2\alpha_r \sin (\delta_1 - \delta_2) = \sin 2\chi
\]

(4) divided by (2):

\[
\frac{2pq \cos (\delta_1 - \delta_2)}{p^2 - q^2} = \frac{(a^2-b^2) \sin 2\beta}{(a^2-b^2) \cos 2\beta}
\]

\[
(7) \quad \tan 2\alpha_r \cos (\delta_1 - \delta_2) = \tan 2\beta
\]

From (6) and (7) it follows:

\[
\cos 2\alpha_r \tan (\delta_1 - \delta_2) = \frac{\sin 2\chi}{\tan 2\beta}
\]

substitution of (5):

\[
\cos 2\alpha_r = \cos 2\beta \cos 2\chi
\]

Now if \( q \) represents the amplitude of the electric vector // to the plane of incidence, and \( p \) represents the amplitude \( \perp \) to the plane of incidence then \( \delta_1 = \delta_\perp \); \( \delta_2 = \delta// + \Delta = \delta// - \delta_\perp \).

Substitution in (5) gives

\[
\tan (-\Delta) = \frac{\tan 2\chi}{\sin 2\beta}
\]

or \( \tan (\pi-\Delta) = \frac{\tan 2\chi}{\sin 2\beta} \)

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7.1. Experimental

The platinum of the optical cell was polished with diamond paste. Thereafter it was subjected to repeated anodic and cathodic treatment.

**Electrolyte:** 0.25 M $\text{H}_2\text{SO}_4$ was prepared from p.a. $\text{H}_2\text{SO}_4$ (Merck) and twice distilled water. 0.1 M $\text{NaOH}$ was made by electrolysis of p.a. $\text{NaOH}$ solution at a mercury cathode; the sodium amalgam was washed and decomposed with twice distilled water to the desired $\text{NaOH}$ concentration. All measurements were performed in a room, which was kept at constant temperature (20.5°C).

**Procedure:** The optical cell was placed on the carrier of the ellipsometer and by means of liquid junction bridges connected with a reference cell ($\text{Pt-H}_2$ electrode in the same solution) and with a counter electrode ($\text{Pt-foil}$). All potentials are given with respect to this reference electrode (fig. 7-1). The potential of the platinum was controlled by a Wenking potentiostat.

First a potential of 200 mV vs H.E. was applied. Oxygen-free $\text{N}_2$ gas was passed through for 20 min. and subsequently blown over the electrolyte during the whole experiment. After

![Fig. 7-1 Arrangement for optical measurements during anodic polarisation of platinum in electrolyte solution.](image-url)
optical alignment of the cell, the optical measurement can begin. The intensity of the reflected light is detected by a Rudolph photomultiplier photometer. Compensator and analyzer (fig.6-2) are rotated until a minimum in the scale reading of the photometer is reached. A very accurate method (7-1) of obtaining the exact extinction settings is to measure \( \lambda/4 \) settings at equal intensities on each side of the minimum. The exact minimum is the average of these two values. Then the compensator is set at this value and two values of equal intensity for the analyzer setting are obtained. This is repeated until the settings no longer vary. The accuracy is \( \pm 0.01^\circ \) for both settings.

The platinum potential is set at increasing anodic values up to 1600 mV. At each potential setting, the corresponding extinction settings of compensator and analyzer are observed.

### 7.2. Results

#### 7.2.1. Potentiostatic measurements in 0.25 M \( \text{H}_2\text{SO}_4 \)

\[ \varphi = 70.9 = 70^\circ 54' \]

<table>
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<th>Pot. (mV)</th>
<th>( \lambda/4 ) plate</th>
<th>Analyzer</th>
<th>( 2 \chi )</th>
<th>( 2 \beta )</th>
<th>( \Delta )</th>
<th>( 2 \psi )</th>
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Fig. 7-2 Graph of $\Delta$ and $2\psi$ as a function of potential in 0.25 M $H_2SO_4$.

Fig. 7-3 Graph of $\Delta$ and $2\psi$ as a function of potential in 0.1 M NaOH.
In Fig. 7.2 \( \Delta \) and \( 2 \psi \) are plotted as a function of anodic potential.

7.2.2. Potentiostatic measurements in 0.1 M NaOH

\[ \theta = 70.9 = 70° 54' \]

<table>
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<tr>
<th>Pot. (mV)</th>
<th>( \lambda/4 ) plate</th>
<th>Analyzer</th>
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<th>( 2 \beta )</th>
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<th>( 2 \psi )</th>
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<tr>
<td>600</td>
<td>71.33</td>
<td>129.13</td>
<td>64° 24'</td>
<td>37° 20'</td>
<td>106° 12'</td>
<td>69° 54'</td>
</tr>
<tr>
<td>700</td>
<td>71.33</td>
<td>129.13</td>
<td>64° 24'</td>
<td>37° 20'</td>
<td>106° 12'</td>
<td>69° 54'</td>
</tr>
<tr>
<td>800</td>
<td>71.40</td>
<td>129.16</td>
<td>64° 29'</td>
<td>37° 12'</td>
<td>106° 12'</td>
<td>69° 56'</td>
</tr>
<tr>
<td>900</td>
<td>71.57</td>
<td>129.32</td>
<td>64° 30'</td>
<td>36° 52'</td>
<td>105° 58'</td>
<td>69° 51'</td>
</tr>
<tr>
<td>1000</td>
<td>71.66</td>
<td>129.37</td>
<td>64° 35'</td>
<td>36° 41'</td>
<td>105° 51'</td>
<td>69° 52'</td>
</tr>
<tr>
<td>1050</td>
<td>71.74</td>
<td>129.45</td>
<td>64° 35'</td>
<td>36° 31'</td>
<td>105° 47'</td>
<td>69° 49'</td>
</tr>
<tr>
<td>1100</td>
<td>71.83</td>
<td>129.54</td>
<td>64° 35'</td>
<td>36° 20'</td>
<td>105° 44'</td>
<td>69° 46'</td>
</tr>
<tr>
<td>1150</td>
<td>71.90</td>
<td>129.56</td>
<td>64° 41'</td>
<td>36° 12'</td>
<td>105° 37'</td>
<td>69° 49'</td>
</tr>
<tr>
<td>1200</td>
<td>71.92</td>
<td>129.58</td>
<td>64° 41'</td>
<td>36° 10'</td>
<td>105° 36'</td>
<td>69° 48'</td>
</tr>
<tr>
<td>1250</td>
<td>72.08</td>
<td>129.73</td>
<td>64° 42'</td>
<td>35° 50'</td>
<td>105° 28'</td>
<td>69° 44'</td>
</tr>
<tr>
<td>1300</td>
<td>72.23</td>
<td>129.85</td>
<td>64° 46'</td>
<td>35° 32'</td>
<td>105° 19'</td>
<td>69° 42'</td>
</tr>
<tr>
<td>1400</td>
<td>72.34</td>
<td>129.97</td>
<td>64° 44'</td>
<td>35° 19'</td>
<td>105° 16'</td>
<td>69° 37'</td>
</tr>
<tr>
<td>1500</td>
<td>72.42</td>
<td>130.03</td>
<td>64° 47'</td>
<td>35° 10'</td>
<td>105° 10'</td>
<td>69° 37'</td>
</tr>
<tr>
<td>1600</td>
<td>72.50</td>
<td>130.07</td>
<td>64° 52'</td>
<td>35° 0'</td>
<td>105° 4'</td>
<td>69° 38'</td>
</tr>
</tbody>
</table>

In Fig. 7-3 \( \Delta \) and \( 2 \psi \) are plotted as a function of anodic potential.

7.3. Calculation of \( \Delta \) and \( \psi \) from the observed ellipsometric settings.

How \( \Delta \) and \( \psi \) are calculated from the observed settings of \( \lambda/4 \) plate and analyzer, will be shown for one pair of values.
\( \lambda/4 \text{ plate } 71^\circ47 \) (centesimal degrees)

\[ \begin{align*}
\text{Analyzer } & 129^\circ14 \\
\theta &= 90^\circ - 71^\circ47 = 18^\circ53 \\
2 \theta &= 37^\circ06 = 37^\circ4' \\
\chi &= (\text{Anal}) - \theta \\
\chi &= (180^\circ - 129^\circ14) - 18^\circ53 = 32^\circ33 \\
2 \chi &= 64^\circ66 = 64^\circ40' \\

\tan (\pi - \Delta) &= \frac{\tan 2x}{\sin 28} = \frac{\tan 64^\circ40'}{\sin 37^\circ4'} \\
\Delta &= 105^\circ55' \\

\cos 2 \alpha_r &= \cos 2 \chi \\
\cos 2 \beta &= \cos 64^\circ40' \cos 37^\circ4' \\
2 \alpha_r &= 70^\circ2' \\
\alpha_r &= \psi \\
2 \psi &= 70^\circ2' \\

\text{The accuracy of the ellipsometer-readings is } \pm 0^\circ.01. \text{ How such a difference of } 0^\circ.01 \text{ in a reading affects the } \Delta \text{ and } 2 \psi \text{ values can be shown most clearly for one set of readings:}

<table>
<thead>
<tr>
<th>\lambda/4 plate</th>
<th>analyzer</th>
<th>\Delta</th>
<th>2 \psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>71.47</td>
<td>129.14</td>
<td>129.13</td>
<td>105^\circ55'</td>
</tr>
<tr>
<td></td>
<td>129.15</td>
<td></td>
<td>105^\circ57'</td>
</tr>
<tr>
<td>71.46</td>
<td>71.46</td>
<td>71.48</td>
<td>105^\circ55'</td>
</tr>
<tr>
<td>71.47</td>
<td>71.47</td>
<td>71.48</td>
<td>105^\circ55'</td>
</tr>
<tr>
<td>71.46</td>
<td>71.46</td>
<td>71.48</td>
<td>105^\circ55'</td>
</tr>
<tr>
<td>71.47</td>
<td>71.47</td>
<td>71.48</td>
<td>105^\circ55'</td>
</tr>
<tr>
<td>71.46</td>
<td>71.46</td>
<td>71.48</td>
<td>105^\circ55'</td>
</tr>
</tbody>
</table>

\text{The accuracy of } \pm 0^\circ.01 \text{ in the ellipsometer readings thus results in an accuracy of } 1'.5.
7.4. Summary of the results

1. The tables show that the ellipsometer readings of $\lambda/4$ plate and analyzer are constant from $0.2 - 0.9$ V in 0.25 M $H_2SO_4$ and from $0.2 - 0.8$ V in 0.1 M NaOH.
   It was elucidated in chapter II that it is generally assumed that no oxygen is present on Pt at potentials of $0.3 - 0.5$V. As was shown in chapter II, Pt is covered with oxygen from $0.9$ V on in 0.25 M $H_2SO_4$. We may thus safely assume that the $\Delta$ and $\psi$ value as calculated for the potential interval $0.2 - 0.9$ V correspond with the bare Pt surface.

2. From 0.9 resp. 0.8 V on, $\Delta$ decreases with potential. From the coulometric measurements we know that an oxygen layer begins to form at these potentials. The presence of an oxygen layer is thus indeed detected by this optical method. The calculation of the optical constants of the layer will be given in the next chapter.

3. In 0.25 M $H_2SO_4$ the slope of $\Delta$ vs potential is $1^0.98 V^{-1}$
   " $2\psi$ " $0^0.50 V^{-1}$
   In 0.1 M NaOH
   " $\Delta$ " $1^0.37 V^{-1}$
   " $2\psi$ " $0^0.36 V^{-1}$

4. The ratio of the slope of the $\Delta-\epsilon_H$ curve with respect to the $2\psi-\epsilon_H$ curve is 3.96 in 0.25 M $H_2SO_4$ and 3.81 in 0.1 M NaOH.

5. The rate of decrease of both $\Delta$ and $\psi$ with potential is smaller in NaOH than in $H_2SO_4$.

6. In chapter II it was found that the curve $Q_C-\epsilon_H$ has a greater slope in sulfuric acid solution than in alkaline solution. Comparison of the coulometric results with the optical results shows that the ratio

$$\frac{\text{slope } \Delta-\epsilon_H \text{ curve in } 0.25 \text{ M } H_2SO_4}{\text{slope } \Delta-\epsilon_H \text{ curve in } 0.1 \text{ M NaOH}} = 1.98$$

$$\frac{\text{slope } Q_C-\epsilon_H \text{ curve in } 0.25 \text{ M } H_2SO_4}{\text{slope } Q_C-\epsilon_H \text{ curve in } 0.1 \text{ M NaOH}} = 1.70$$

is equal to the ratio:

$$\frac{\text{slope } \Delta-\epsilon_H \text{ curve in } 0.25 \text{ M } H_2SO_4}{\text{slope } \Delta-\epsilon_H \text{ curve in } 0.1 \text{ M NaOH}} = 1.37$$

$$\frac{\text{slope } Q_C-\epsilon_H \text{ curve in } 0.25 \text{ M } H_2SO_4}{\text{slope } Q_C-\epsilon_H \text{ curve in } 0.1 \text{ M NaOH}} = 1.18$$

The implication is that $(\Delta_L-\Delta)$ is proportional to $Q$. 79
7. From the coulometric measurements we know that a monolayer of oxygen is formed at 1.4 V during potentiostatic anodization. Thus even though the surface coverage amounts to less than a monolayer, the ellipsometer detects the presence of a layer. The observed changes in the polarization state thus give an averaged picture of the situation at the surface. When e.g. $\theta = 0.5$ this means that 50% of the surface is covered. This appears to result in one set of values for $\lambda/4$ plate and analyzer.

REFERENCES

CHAPTER VIII

THE OPTICAL CONSTANTS OF THE ANODIC FILM ON PLATINUM

8.1. Determination of the refractive index of Pt II- and Pt IV- oxide.

If the oxygen layer on Pt is an oxide layer, then we would like to compare its refractive index as obtained with the ellipsometer, with the refractive index of platinum-oxide. No refractive index data are given in the literature for any of the oxides of platinum. Therefore the refractive index of Pt II- and Pt IV- oxide were determined. The platinum oxides PtO·H₂O and PtO₂·4H₂O were prepared according to WOHLER (8-1).

Preparation of PtO₂·4H₂O.
To a dilute solution of K₂PtCl₆ excess 10% NaOH is added. The solution is boiled for 30 min., cooled and then neutralized with acetic acid. The yellow coloured PtO₂ hydrate precipitates and is filtered off.

Preparation of PtO·H₂O.
SO₂ is passed through a dilute solution of K₂PtCl₆ in order to reduce PtCl₆⁻ to PtCl₄⁻. A calculated amount of NaOH is added; the solution is boiled and black PtO hydrate precipitates. The whole preparation is carried out in CO₂ atmosphere.

The refractive indices were determined with the immersion method (8-4): The crystal is bedded in a liquid or glass medium of known refractive index. Under the microscope is observed in which direction the bright boundary line around the crystal moves when the microscope is put out of focus. From this it follows whether n_crystal is higher or lower than n_medium.

For the determination of the refractive index of PtO₂·4H₂O, reference media were used, which were composed from arsenic tribromide, sulphur and arsenic disulfide. White light was used. According to MEYROWITZ & LARSEN (8-2) the refractive index of this
mixture lies between 1.82 and 2.00 depending on the composition.

For the determination of the refractive index of PtO.H_2O melts of TlBr and TlI were used as reference media (sodium light). The refractive index of these melts ranges from 2.4 to 2.8 (BARTH (8-3)).

For the refractive indices was found:

\[
\begin{align*}
1.970 < n & < 1.979 \\
PtO_2.4H_2O \\
2.60 < n & < 2.65 \\
PtO.H_2O
\end{align*}
\]

8.2. Calculation of the optical constants

The values of \(\Delta\) and \(2\psi\) in the potential region 200-900 mV remain constant and therefore they are considered to be the values corresponding with the bare platinum surface. These values are substituted in eq. 17a and 17b of chapter V and \(n_2\) and \(K_2\) are calculated. From these values, \(a_2\) and \(a_2'\) are obtained.

\[
\begin{align*}
a_2 &= -0.033 \\
a_2' &= +0.032
\end{align*}
\]

whereby \(n_2^{20}\) of 0.25 M H_2SO_4 = 1.337 and \(n_2^{20}\) of 0.1 M NaOH = 1.335.

The equations relating \((\Delta_L-\Delta)\) and \((2\psi_L-2\psi)\) with \(L, n_1, K_1\) of the layer, consist of 2 sets of equations, namely (22) and (23) for a non-absorbing layer \(K_1 = 0\); (27) and (28) for an absorbing layer \(K_1 \neq 0\).

Comparison of these two sets of equations shows that only in the case of a non-absorbing layer, both the layer thickness \(L\) and its refractive index \(n_1\) can be obtained from the measured values of \((\Delta_L-\Delta)\) and \((2\psi_L-2\psi)\). We shall first consider a non-absorbing layer.

8.2.1. Case \(K_1 = 0\)

Since \(a_2 < 0\), it follows from eq. (22) that \((\Delta_L-\Delta)\) will always be \(< 0\) for \(n_1 > n_0\), that is to say, \(\Delta\) decreases with increase of \(L\). The graphs 7-2 and 7-3 show that both \(\Delta\) and \(2\psi\) decrease with increasing potential. In order that \((2\psi_L-2\psi) < 0\), it follows from eq. (23) that

\[
n_0^2 \left(\frac{1}{n_1^2} - a_2\right) < (\cos^2 \phi - a_2n_0^2)
\]
or

\[
\frac{n_0^2}{n_1^2} < \cos^2 \theta
\]

For \( \theta = 70^\circ \), this implies that \( n_1 > 4.3 \). Thus a \( n_1 \)-value greater than 4.3 is to be expected.

Substitution of \( \frac{d(A_L-\Delta)}{dc} = -1^\circ .98 \text{ v}^{-1} \)

and \( \frac{d(2\psi_L-2\psi)}{dc} = -0^\circ .50 \text{ v}^{-1} \)

in eq. (22) and (23) yields

\( n_1 = 8.7 \)

and \( \frac{dL}{dc} = 1.51 \text{ \AA} \text{ v}^{-1} \)

(1° \( \Delta \) corresponds with 0.76 \( \text{\AA} \)).

This value of \( n_1 \) is extremely high and therefore unlikely. Moreover it would imply that the thickness of a monolayer is 0.84 \( \text{\AA} \), which is improbable.

8.2.2. Case \( K_1 \neq 0 \)

At first sight it seems to be an insoluble problem, since we have two equations (27) and (28) with 3 unknown entities \( L, n_1, K_1 \). This problem can only be solved if either \( L \) or the refractive index \( n_1 \) of the layer can be obtained by other means. \( L \) can be found from the coulometric quantity of oxygen on platinum. The refractive index \( n_1 \) was measured for chemically prepared platinum oxides.

8.2.2.1 Substitution of \( L \)

The coulometric quantity \( Q_c \) of oxygen on platinum was measured by cathodic stripping. Details are given in chapter II. Taking into account the roughness factor, the slope of the curve \( Q_c \) vs potential is given by:

\[
\frac{dQ}{dc} = 0.90 \text{ mC.cm}^{-2}.\text{v}^{-1} \text{ in } 0.25 \text{ M } \text{H}_2\text{SO}_4
\]

\[
\frac{dQ}{dc} = 0.63 \text{ mC.cm}^{-2}.\text{v}^{-1} \text{ in } 0.1 \text{ M } \text{NaOH}
\]
The thickness \( L \) is obtained from \( Q \) as follows

\[
L = \frac{Q \times M}{S \times d \times n \times F}
\]

in which

- \( M \) = molecular weight
- \( d \) = density
- \( n \) = number of electrons
- \( F \) = Faraday's number
- \( S \) = surface area

Assuming that the anodic layer is Pt II oxide, with \( d_{\text{PtO}} = 14.9 \) \((\text{Handbook of Chemistry and Physics})\), we get

\[
\frac{dL}{d\varepsilon} = 6.6 \ \Omega \ \text{V}^{-1} \ \text{for} \ 0.25 \ \text{M H}_2\text{SO}_4
\]

\[
\frac{dL}{d\varepsilon} = 4.6 \ \Omega \ \text{V}^{-1} \ \text{for} \ 0.1 \ \text{M NaOH}
\]

The observed variation of \( \Delta \) and \( 2\psi \) with potential is reported in chapter VII as

\[
\frac{d(\Delta_L-\Delta)}{d\varepsilon} \ \text{resp.} \ \frac{d(2\psi_L-2\psi)}{d\varepsilon}
\]

According to eq. (27) and (28)

\[
\frac{d(\Delta_L-\Delta)}{d\varepsilon} = \frac{4\pi}{\lambda} \ \sin^2 \phi \ \cos \phi \ \frac{n_o^7}{(\cos^2 \phi - a_2 n_o^2)^2 + a_2' n_o^2} \ \frac{P}{(a_1^2 + a_1'^2)} \ \frac{dL}{d\varepsilon}
\]

\[
\frac{d(2\psi_L-2\psi)}{d\varepsilon} = -\frac{4\pi}{\lambda} \ \sin 2\psi \ \frac{\sin^2 \phi \ \cos \phi \ n_o^7}{(\cos^2 \phi - a_2 n_o^2)^2 + a_2' n_o^2} \ \frac{N}{(a_1^2 + a_1'^2)} \ \frac{dL}{d\varepsilon}
\]

whereby the assumption is made that \( a_1 \) and \( a_1' \) do not vary with potential. Substitution yields \( P \) and \( N \).

\( P \) and \( N \) are a function of \( \phi, a_o, a_1, a_1', a_2, a_2' \), \( \phi, a_o, a_2 \) and \( a_2' \) are known quantities.

For these values of \( \phi, a_o, a_2, a_2' \), tables were computed* with an

*) Thanks are due to the Mathematical Department for these calculations.
IBM 1620 computer for

\[ \frac{P}{(a_1^2 + a_1')^2} \quad \text{and} \quad \frac{N}{(a_1^2 + a_1')^2} \]

for varying \( n_1 \) and \( K_1 \) values.

\( n_1 \) was varied from 1.7 to 4.0 with intervals of 0.1 and for each value of \( n_1 \), \( K_1 \) was varied from 0 to 2.0 with intervals of 0.1.

The \( P \) and \( N \) value, obtained from the experimental data are then looked up in the computed \( P \) and \( N \) tables in order to find the corresponding \( n_1 \) and \( K_1 \). This gives for 0.25 M \( H_2SO_4 \) and for 0.1 M NaOH:

\( n_1 = 3.0 \quad \text{and} \quad K_1 = 0.5 \)

\( n_1 = 3.0 \quad (1 - 0.5 \, i) \)

If the layer is a Pt IV-oxide layer \( (d_{PtO_2} = 10.2) \), then

\[ \frac{dL}{d\varepsilon} = 5.20 \, \text{Å}. \, \text{V}^{-1} \] in 0.25 M \( H_2SO_4 \)

\[ \frac{dL}{d\varepsilon} = 3.63 \, \text{Å}. \, \text{V}^{-1} \] in 0.1 M NaOH.

This yields for both electrolyte solutions:

\( n_1 = 3.9 \quad \text{and} \quad K_1 = 0.3 \)

\( \tilde{n}_1 = 3.9 \quad (1 - 0.3 \, i) \)

Graph 7-2 shows that \( \psi_L - \psi \) is about constant in 0.25 M \( H_2SO_4 \) from 0.9 - 1.2 V. For this region we calculate \( n_1 = 2.8 \, K_1 = 0.3 \) if a Pt II-oxide layer is assumed and \( n_1 = 3.6 \); \( K_1 = 0.3 \) if a Pt IV-oxide layer is assumed.

REDDY and BOCKRIS (8-5) assumed at first a value \( n_1 = 2.1 \) in order to calculate the thickness of an anodic film on Pt in 1 N \( H_2SO_4 \). From computer analysis REDDY, GENSHWAW and BOCKRIS (8-6) conclude to \( n_1 = 3.3 \) for the real part of the refractive index.

Comparison of our computed \( n_1 \) value with the bulk values shows that the calculated value \( n_1 = 3.0 \) is in reasonable agreement with \( n = 2.6 \) for bulk Pt II-oxide. The calculated value \( n_1 = 3.9 \) differs considerably from the value \( n = 1.97 \) for bulk Pt IV-oxide.

A monolayer of oxygen is equivalent to 0.48 mC.cm\(^{-2}\). With eq. (1) for Pt II-oxide, we calculated for the thickness of a monolayer \( L = 3.5 \, \text{Å} \), this value is very likely.

Actually the refractive indices of bulk Pt II- and Pt IV-oxide refer to Pt0.H\(_2\)O respectively to Pt0\(_2\).4 H\(_2\)O. The refractive index
of the anhydrous-oxides will be somewhat higher and we calculated approximately $n = 2.9$ for bulk PtO and $n = 2.5$ for bulk PtO$_2$. The large discrepancy for Pt IV-oxide remains, while the agreement for Pt II-oxide is even better.

With eq. (1) $Q$ was transformed to $L$ by assuming that the layer was an oxide layer.

If the oxygen layer on platinum is an adsorbed oxygen layer, we may calculate $L$ from $Q$ by assuming that the thickness of a monolayer of oxygen is $3 \, \AA$. This gives for the optical constants of the layer

$$n_1 = 3.5 \, (1 - 0.4 \, i).$$

This high value of $n$ indicates that we are dealing here indeed with an oxide film, since such a high value is not very likely for adsorbed oxygen.

KRUGER and AMBS (8-7) found $n = 1.25$ for a thin film of condensed O$_2$ on gold at 4.2°K. KRUGER (8-8) suggests that it is probable that also in other cases the refractive index of adsorbed oxygen is about 1.25. Therefore we may conclude that the anodic film on platinum is a Pt II-oxide layer.

8.2.2.2. Substitution of $n_1$

Now we could also plug in the measured value of the refractive indices of the bulk-oxide. In section 8-1 the refractive indices of the oxides of Pt II and Pt IV are given. Substitution of $n_1 = 2.6$ gives:

$$K_1 = 0.6$$

$$\frac{dL}{dr} = 7.1 \, \AA \, V^{-1}$$

Substitution of $n_1 = 2.0$ gives:

$$K_1 = 0.6$$

$$\frac{dL}{dr} = 7.5 \, \AA \, V^{-1}$$

*) These calculated values for the refractive index of the anhydrous-bulk-oxides may only be considered as approximate values. They were calculated from the values of $n$ of the bulk-oxides with bound water using the LORENZ formula

$$\frac{n^2 - 1}{n^2 + 2} \, d = \text{constant}$$

We mention these values here only to give some idea to what extent it would affect the data.
Again we see a good agreement for $\frac{dL}{dx}$ with $\frac{dL}{dx}$ value calculated from $Q_c$ for Pt II-oxide.
The agreement of $\frac{dL}{dx}$ with $\frac{dL}{dx}$ calculated for Pt IV-oxide is less.

In the derivation of the formulas (22), (23), (27), (28) it is assumed that the refractive index of the layer does not change with thickness. Section 8.3 will deal with the refractive index of thin films as compared with the bulk value.

8.3. Refractive index of thin films

Several authors have observed that the optical experiments at very thin metal films yield $n$ and $K$ values that differ from the bulk $n$ and $K$ values. In order to explain this phenomenon, Maxwell developed a theory in which a very thin film is considered to consist of spherical metal particles of refractive index $n_1$, distributed at random in a medium of refractive index $1$. The particles are small compared with the film dimensions. One can therefore say that the metal spheres occupy a volume fraction $q$ of the film. The effective refractive index is $n_e$. Maxwell calculates:

$$\frac{n_e^2 - 1}{n_e^2 + 2} = q \frac{n_1^2 - 1}{n_1^2 + 2}$$

This relation appears to give a reasonable agreement with measurements on thin metal films (cf Heavens (8-10); Mayer (8-9)). For $n_1$ the bulk value is taken, $q$ appears to be about 0.6 for most cases.

All these experiments show that with decrease of film-thickness, $n_e$ increases and $K_e$ decreases with respect to the bulk value. So for these films $n_e > n_{\text{bulk}}$; $K_e < K_{\text{bulk}}$. We want to point out that this is not necessarily implied by eq. (2). For instance we have calculated $n_e$ and $K_e$ for $n_1 = 2$ and $q = 0.6$ for some values of $K_1$. Fig. 8-1 shows that it depends on the value of $K_1$ whether $n_e > n_1$.

Odelevsky (8-11) has pointed out that eq. (2) is not correct because the particles of refractive index $n_1$ are not present in a medium $n = 1$ but in a medium with the effective refractive index $n_e$; thus the film with effective refractive index $n_e$ consists of particles which occupy a volume fraction $q_1$, the rest of the film is air.
The rule of ODELEFSKY for a mixture of spherical particles $i$ with dielectric constant $\varepsilon_i$ in a medium $\varepsilon$ is given by

$$\sum q_i \frac{\varepsilon_i - \varepsilon}{\varepsilon_i + 2\varepsilon} = 0$$

If we consider one species of refractive index $n_1$ occupying a volume fraction $q$ while the rest of the film has a refractive index $n_e$ then it follows from eq. (3) that the effective refractive index $n_e$ is related to $n_1$ and $n_o$ as given in (4).

$$\frac{n_e^2 - n_o^2}{3 n_e^2} = q \frac{n_1^2 - n_o^2}{n_1^2 + 2 n_e^2}$$

In view of this, it is very likely that also the values of $n_1$ and $K_1$ for the anodic film on Pt have to be modified. The calculated values $n_1 = 3.0$ and $K_1 = 0.5$ must then be the effective refractive index and the effective absorption index.

In (4) are substituted:

$$n_e = 3.0 \quad K_e = 0.5 \quad n_o = 1.34 \quad n_1 = 2.6.$$ 

Assuming $q = 0.6$ we thus obtain the bulk value of $K_1$

$$K_1 = 0.9.$$ 

8.4. Discussion

a. The calculations show that the refractive index of the anodic layer agrees reasonably with the refractive index of bulk Pt II-oxide. Thus the layer formed on platinum during
anodization from 0.9 to 1.7 V is most likely a Pt II-oxide layer. The thickness of this film increases with 6.6 Ω V⁻¹ in 0.25 M H₂SO₄, at 1.6 V L = 5 Å. In 0.1 M NaOH $\frac{dL}{dc} = 4.6 Ω V⁻¹$, and L = 4.4 Å at 1.6 V. For such a thin layer the term "chemisorption" as well as "oxide" applies, but it is without meaning to make a clear cut distinction between the two terms.

In chapter I we have pointed out that from the literature data, the conclusion might be drawn that at low current-densities the formation of Pt II-oxide is most likely. This is confirmed by the experiments presented above.

b. Besides the refractive index $n_1$ also a value for $K_1$ the absorption index is obtained. As was shown in section 8.3 the value of $K_1$ for bulk oxide may be expected to be higher than 0.5. A value $K_1 = 0.9$ was calculated. In fact this gives an interesting information concerning the nature of the layer. It was shown in chapter V that K is closely connected with the conducting properties of the material:

$$n^2 K = \frac{\mu \sigma}{v}$$

with $\mu$ = permeability

$\sigma$ = specific conductivity, which is frequency dependent.

Metals are good electronic conductors, the K-values are high: between 1 and 3. Purely ionic conductors as e.g. Al₂O₃ are non-absorbing: $K = 0$.

The reported $K_1$ value thus means that the anodic film on platinum is a good electronic conductor. This is in agreement with what is to be expected. A platinum electrode acting as anode in electrolyte solution namely can easily transfer electrons across this film so that the oxidation of H₂O to O₂ will proceed.

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LIST OF SYMBOLS

$a_X$  activity of substance X

$a_0 = \frac{1}{n_0}$

$a_1 = \frac{1-K_1}{n_1(1+K_1)^2}$

$a_1' = \frac{2K_1}{n_1(1+K_1)^2}$

$a_2 = \frac{1-K_2}{n_2(1+K_2)^2}$

$a_2' = \frac{2K_2}{n_2(1+K_2)^2}$

$A$  amplitude of the incident light

$c_X$  concentration of substance X

$C$  differential capacity

$d$  density

$E$  magnitude of the electric vector $\mathbf{E}$

$F$  Faraday's number

$f$  proportionality constant

$G$  free energy

$H$  magnitude of the magnetic vector $\mathbf{H}$

$I$  current

$i = \sqrt{-1}$

$J$  current density, i.e. current with respect to geometrical electrode-area

$J_O$  exchange current density

$k$  specific rate-constant

$K$  absorption-index

$L$  thickness
\[ \ln a = e^{\log a} \]
\[ \log a = 10^{\log a} \]

M: molarity
N: normality

N: function of \( \varphi, a_0, a_1, a_1', a_2, a_2' \) (see chapter V)

n: number of electrons exchanged in electrode reaction

n: refractive index

P: gas pressure

P: function of \( \varphi, a_0, a_1, a_1', a_2, a_2' \) (see chapter V)

Q: amount of electricity per geometric electrode area

q: volume fraction

R: gas constant

R_i: amplitude of reflected light

r: Fresnel-coefficient for reflected light

RF: roughness factor

S: surface area

t: time

\( t_{//} \): Fresnel coefficients for transmitted light

T: temperature \( ^{\circ} \)K

\( T_{//} \): amplitude of transmitted light

\( v_o \): velocity of light in vacuum

\( v_1 \): velocity of light in medium 1

\( \alpha \): symmetry factor

\( \alpha \): angle between plane of vibration and normal to plane of incidence

\( \beta \): angle between major axis of ellips and normal to the plane of incidence

\( \delta \): phase change

\( \Delta \): relative phase-retardation \( \Delta = \delta_{//} - \delta_{\perp} \)

\( \epsilon \): electrode potential with respect to N.H.E.

\( \epsilon_H \): electrode potential with respect to reversible hydrogen electrode in the same solution

\( \epsilon_0 \): standard reversible potential with respect to N.H.E.

\( \epsilon_{rev} \): reversible potential with respect to N.H.E.

\( \epsilon \): dielectric constant

\( \theta \): fractional surface coverage

\( \mu \): magnetic permeability

\( \nu \): frequency

\( \lambda \): wave length

\( \rho \): electric charge density

\( \rho \): reflection coefficient
specific conductivity

angle between normal to plane wave and normal to boundary

relative amplitude diminution of the // and \ perpendicular component of the reflected light

angular velocity

ellipticity

Subscript \( i, r, t \) denotes incident, reflected, transmitted

Subscript //, \( \perp \) denotes component of light parallel // resp. perpendicular \( \perp \) to plane of incidence

Subscript A denotes anodic

Subscript C denotes cathodic

Subscript ad denotes adsorbed

N.H.E. : standard hydrogen electrode

H.E. : hydrogen electrode in the same solution

LIST OF UNITS

A ampère

Å angstrom

C coulomb

F farad

V volt

Ω ohm
Several oxides of platinum are known, some of these have been prepared electrochemically. In chapter I a literature review is given. The potential of the redox couple PtO\textsubscript{2}^-PtO and of the couple PtO-Pt lies in the potential region in which an anodic oxygen film is formed on platinum. Therefore several authors have concluded that PtO and PtO\textsubscript{2} are formed during anodization, whereas others suppose that oxygen is only chemisorbed on Pt. This anodic film is the subject of this investigation.

The quantity of oxygen (Q) that is formed on Pt by potentiostatic anodization is determined by coulometric measurements (chapter II). Q increases linearly with potential in the potential region 0.9 - 1.7 V vs H.E. in 0.25 M H\textsubscript{2}SO\textsubscript{4} respectively 0.8 - 1.7 V vs H.E. in 0.1 M NaOH. The rate of increase of coverage with potential was found to be greater in 0.25 M H\textsubscript{2}SO\textsubscript{4} than in 0.1 M NaOH. At 1.4 V a monolayer is reached. The rate of formation of this oxygen layer depends on the anodic potential (chapter III). At 1.2 to 1.6 V the rate is determined by

\[ J = k' c_{\text{red}} \exp \frac{anF}{RT} \epsilon \exp - \gamma f \theta \]

with \( a, \gamma \) = symmetry factor
\( n \) = number of electrons exchanged per reaction
\( k' \) = specific rate constant
\( c_{\text{red}} \) = concentration of red. component
\( \epsilon \) = electrode potential
\( f \) = proportionality factor
\( \theta \) = fractional coverage.

This "Temkin" relation implies that with increasing surface coverage at constant potential the reaction proceeds slower with time.

Beyond 1.6 V a diffusion process appears to be rate determining.
The oxygen layer plays also the decisive role in order that

\[ 2 \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \]

becomes the potential determining reaction. (chapter IV)

The conditions that must be fulfilled to obtain the reversible potential of this reaction were established. The potential of \( \epsilon_H = 1.23 \text{ V} \) can be observed on Pt in carefully purified 0.25 M \( \text{H}_2\text{SO}_4 \) or 0.1 M NaOH if Pt is anodized and thereafter exposed to \( \text{O}_2 \) gas for at least 15 hours. This implies that the reaction (1) proceeds on an oxygen film. As long as this oxygen film is being formed, a mixed potential will be observed. Reaction (1) will be the potential determining reaction as soon as the rate of the build-up process has slowed down to values below the exchange-current density of reaction (1). This implies that its ionic conductance is reduced and that the film is mainly electronic conducting. In order to get more insight concerning the nature of this anodic film on Pt, an optical method is used.

The method is based on the change in polarization state of incident linearly polarized light by reflection on a metal surface. The optical parameters that are measured are the relative phase retardation \( \Delta \) and the relative amplitude diminution \( \psi \) of the two components // and \( \perp \) to the plane of incidence. When a layer is present on this metal surface both \( \Delta \) and \( \psi \) undergo a change. The magnitude of this change in \( \Delta \) and \( \psi \) is for thin layers proportional to the thickness \( L \) of the layer and is further a function of the refractive index \( n_1 \) and the absorption index \( K_1 \) of the layer.

\[
\Delta_L - \Delta = f_1 (\phi \lambda n_o n_1 K_1 n_2 K_2 L)
\]
\[
\psi_L - \psi = f_2 (\phi \lambda n_o n_1 K_1 n_2 K_2 L)
\]

Index \( L \) denotes the thickness of layer \( L \) which covers the surface.

- \( n_o \) = refractive index of surrounding medium
- \( \phi \) = angle of incidence
- \( \lambda \) = wave length
- \( n_2, K_2 \) = optical constants of the metal (chapter V).

The optical measurements were performed with a Rudolph Ellipsometer (chapter VI) on Pt immersed in 0.25 M \( \text{H}_2\text{SO}_4 \) or in 0.1 M NaOH. By means of a potentiostat a constant potential was applied to the Pt anode, and \( \Delta \) and \( \psi \) were determined as a function of this potential in the potential region 0.2 - 1.7 V vs H.E.

With increasing potential \( \Delta \) and \( \psi \) remain at first constant up to
0.9 V in acid solution and to 0.8 V in alkaline solution. From these potentials on, $\Delta$ decreases linearly with potential. Since also $Q$ increases with potential, this means that $\Delta_L - \Delta$ is proportional to $Q$ (chapter VII). The rate of decrease of $\Delta$ with potential is greater in acid than in alkaline solution.

Section 8.1 deals with the determination of the refractive indices of the chemically prepared Pt-oxides. It was found that Pt II-oxide has a refractive index 2.6 and Pt IV-oxide 2.0. Calculation of the optical constants of the anodic film shows that the anodic film is absorbing: $n_1 = 3.0 (1-0.5 i)$ (Chapter VIII). This value of $n_1$ appears to be in reasonable agreement with the refractive index of Pt II-oxide.

The observed value of the absorption index $K_1$ indicates moreover that this anodic film on platinum is a good electronic conductor indeed.
CURRICULUM VITAE


STELLINGEN

1. Mc Gowan heeft de hydrolyse constante pK van een aantal metaal ionen $X^{m+}.y H_2O$ berekend met behulp van een door hem opgestelde formule. Aangezien het niet vaststaat dat deze formule algemeen geldig is, is het niet gerechtvaardigd om uit verschillen in berekende en experimenteel bepaalde pK waarden conclusies te trekken over het hydratatie getal y.


2. Bij de oxidatie van een jodide- en jodiumoplossing in dimethylsulfoxide schrijven Giordano c.s. de tweede anodische trap in de stroomspanningscurve ten onrechte toe aan de oxidatie van $I_3^-$ tot $I_2$.


3. Voor de gasdiffusie elektroden, die werken volgens het "Will" principe, zullen, voor de hoge temperatuur brandstofcel, mechanisch vervaardigde systemen te prefereren zijn boven poreuze sinterlichamen.


F.A. Schneider Voordracht gehouden op "Journées internationales d'etude des piles à combustible" S.E.R.A.I. Brussel, juni 1965.

4. Krutenat en Uhlig constateren dat na electrolyse in 0.1 M NaCl met Pt, Ni of Sn kathode een "tijdelijk reducerende" stof in de katholyt aanwezig is. Tegen hun conclusie dat deze stof opgeloste atomaire waterstof is, zijn bezwaren aan te voeren.

5. De adsorptie van CO aan wolraam is bestudeerd m.b.v. veldion-microscopie en veldelectron-microscopie. De interpretatie van de experimentele resultaten zoals deze gegeven wordt door HOLSCHER en SACHTLER verdient de voorkeur boven die van EHRLICH.


6. Volgens REPIANSKII wordt de kinetica van het oplossen van een metaal in HNO₃ bepaald door de waarde van de standaard potentiaal. Voor de corrosie-snelheid is echter ook de uitwisselingsstroomdichtheid van anodische en kathodische reactie bepalend.


7. BRONSTED'S theorie over de invloed van de ionsterkte op de snelheid van een ionen-reactie wordt door KORTUM behandeld voor de reactie tussen Fe³⁺ en I⁻. Daarbij neemt KORTUM ten onrechte aan dat de snelheid van de reactie bepaald wordt door (FeI)^{2+} + Fe^{2+} + I⁻.


Eindhoven, 25 april 1967 W.H.M. Visscher