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Optical Methods in Corrosion-electrochemical Studies

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The review discusses problems relating to the technique of optical measurements on the surface of a metallic electrode in an electrolyte solution. Methods for the measurement of the thickness of oxide films on the electrode surface and of the extent of adsorption at the metal-electrolyte interface are examined.
A number of examples of spectroscopic studies on metal-electrolyte and metal-oxide-electrolyte systems are quoted. The usefulness of optical methods for the investigation of the processes on the surface of a metallic electrode in solution is demonstrated on the basis of the data presented.
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I. INTRODUCTION

The extension and deepening of our knowledge of corrosion processes requires new research techniques. This was already noted in a recently published paper by Bockris et al.[1], who considered the necessity of applying a number of non-electrochemical methods to investigate the electrode surface (phase contrast, interferometric, ellipsometric, and Mössbauer spectroscopic methods).

Indeed many very important corrosion problems, for example inhibition of corrosion, and passivity, require the consideration of adsorption processes and of interactions at a molecular level and hence new methods for the investigation of the electrode surface are needed, since traditional electrochemical techniques do not yield the required information. Methods permitting measurements without disrupting the initial electrochemical system are of greatest value.

Many optical methods meet these requirements. Optical studies can be made directly in the cell for corrosion experiments. The perturbation introduced into the electrochemical system by the light beam may be minimal and, moreover, the absence of measurable photoeffects can serve as a criterion of the smallness of this perturbation. Finally, physical optics, which has been developing vigorously during the last two decades, has now provided fairly powerful theorectical and experimental techniques.

In this review we shall consider certain optical methods for the investigation of a solid electrode in an electrolyte solution, disregarding optical microscopic observations of the surface and optical methods for the analysis of the composition of the solution.

The interaction of an electromagnetic wave and matter, including solids, results in a change of the amplitude and phase of the wave. It is readily seen that this interaction can be described (on the basis of the law of conservation of energy) by means of the universal relation

$$K + R + M = 1 , \qquad (1)$$

where K, R, and M are the coefficients of absorption, relection, and scattering respectively. Thus the study of the changes in any of these coefficients can yield useful information about the properties of the test substance †.

† In the case of specular reflection, scattering may be neglected.

Since metals absorb light strongly over a wide spectral range and their transmittance (absorbance) can be studied only for very thin films ($\leq$ 100 Å), it is clear that the optical methods for the investigation of changes in the electrode surface as a result of electrochemical reactions are mainly those employing the changes in the amplitude-phase parameters of the light reflected from the electrode.

Since in examining corrosion-electrochemical problems we are interested primarily in a number of surface parameters, the optical methods will be classified from this point of view.

II. MEASUREMENTS OF THE THICKNESS OF OXIDE FILMS FORMED ON THE ELECTRODE SURFACE

When the problem of the measurement of the thickness of oxide films on a metallic support is considered, it becomes immediately clear that many optical methods[2-6] are unsuitable for such measurements, since they require the presence of a partly uncoated support and a sharp step at the place where the film terminates.

Many metals (mainly the so called "rectifying metals") form films on anodic oxidation, which give rise to bright interference colours, arising from the partial reflection and refraction of the light incident on the oxide surface. The phase difference between the beams leading to interference is due both to the difference in the paths traversed by the beams and the phase difference arising on reflection. The phase change on reflection is different for the p- and s-components of the light beam (the electric vector of the p-beam is parallel and that of the s-beam is perpendicular to the plane of incidence) except for the case where the beam is incident on the surface at right angles. However, this difference is negligibly small for small angles of incidence: $\alpha \leq 10-15°$.

The simplest interference method for the determination of the thickness of oxide films on metals is based on a comparison of the colour of the film with that of a thin layer of air viewed in transmitted light. The thickness of the air layer must be divided by the refractive index of the material of the film. A very extensive and fairly accurate table of colours of air films was compiled by Rollet[7] and certain additions were made by Menh[8]. However, one must bear in mind that this table was compiled with a number of simplifying assumptions. Firstly, no account is taken of the

dispersion of the refractive index[9]. Secondly, it is assumed that the phase shifts at the boundaries of the layer are zero or π. However, for oxide layers on a metal, the phase shift at one boundary is characteristic of the metal and differs from both zero and π. According to the theory quoted in Methfessel's review[10], the intensity of the light reflected at right angles from a plate has minima corresponding to the thicknesses (d) and wavelengths (λ) which satisfy the relation

$$d = \left(q + \frac{\pi - \delta}{2\pi}\right)\frac{\lambda}{2n} \quad , \qquad (2)$$

where $\delta = \delta_1 - \delta_2$, δ_1 and δ_2 being the phase shifts on reflection from the front and rear surfaces of the film. For an oxide layer on a metal, we evidently have $\delta_1 = \pi$ and $\delta_2 = \delta_m$. The expression for δ_m can be derived from Fresnel's formulae:

$$\tan\delta_m = \frac{-2n_0k}{n^2 + k^2 + n_0^2} \quad , \qquad (3)$$

where k is the absorption coefficient of the metal, n_0 the refractive index of the medium traversed by the light beam, and n the refractive index of the oxide film;

$$q = \frac{\varepsilon}{2\pi} \quad , \qquad (4)$$

where ϵ is the phase difference determined solely by the difference between the optical path lengths. Estimates of the accuracy of this method quoted in Methfessel's review[10] showed that the error in determining the thickness of the layer (the thickness of a layer of silver iodide and silver was calculated) is about 200 Å towards higher values. Thus this method is applicable, if at all, to comparatively thick films giving several interference series. The unsuitability of this method for thin films was demonstrated by the present authors[11] in relation to anodic films on titanium obtained in a dilute solution of alkali. Moreover, both the present authors' investigation and others[10] show that the sequence and tints of the oxide film colours frequently disagree with Rollet's table. This shows that the formation of the film colour can depend on the structure of the film itself.

The fastest and most accurate method employing interference phenomena‡ is the spectrophotometric determination of the wavelengths giving the reflectance minima for a fixed angle of incidence of the light. Fig. 1, taken from Young's review[12], presents a curve of this kind. It shows that the wavelength at the minimum can be determined with a high degree of accuracy. It has been stated[13] that the thickness of the film and the refractive index can be determined in this way to within 1% or better. The accuracy in the determination of the refractive index n and hence of the thickness of the film is said[13] to be related to the error in the measurement of the reflectance R by the formula

$$\frac{dn}{n} = \frac{R^{1/2}}{2(1-R)}\frac{dR}{R} \quad . \qquad (5)$$

If n is known, the geometrical thickness of the film can be determined from the optical thickness corresponding to the singular point on the reflectance curve. It is then necessary to determine the interference series for the observed bands and to take into account the dispersion of the film. One should note that the dispersion of the film will have a significant influence only for thin films (single interference series). Abelès showed for a zinc sulphide film[14] that neglect of dispersion increases the error in the determination of the thickness of the film to 12%.

‡ When absorption of light by the film may be neglected.

A spectrophotometric method for the investigation of anodic films was used by Ellis[15] in a somewhat modified form. The applicability of this method and its great potentialities were confirmed by a recent study[16] whose authors investigated the kinetics of the growth of the oxide on a uranium electrode in an alkaline medium. A fairly rigorous theory of the application of interferometric methods is described by Winterbottom[17] and Heavens[13]. Heavens[13] reviews certain special interferometric methods such as polarisation interferometry and multibeam interferometry.

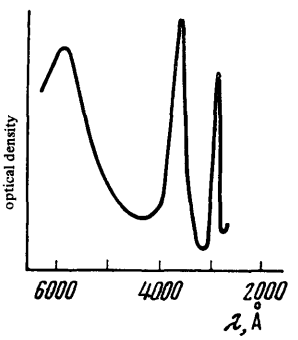


Figure 1. Spectrophotometric curve illustrating the interference minima and the reflection maxima for an oxide film on tantalum. The film is sufficiently thick to obtain several interference series[12].

Apart from studies by reflected light, transmittance measurements can be used to determine the thickness of oxide films. In this case one employs thin semitransparent layers of the metal and the change (increase) in the transmittance of this layer on oxidation is investigated. Light which is not absorbed by the oxide is employed. This method was developed long ago by Steinheil[18], who used it to investigate the oxidation of aluminium. By combining transmittance measurements with reflectance measurements on opaque metallic films *in vacuo* and in air, Hass and coworkers[19-21] established that stable films, formed spontaneously on aluminium in air, have a thickness between 30 and 40 Å and those on titanium are 35 Å thick.

Fig. 2 presents data obtained by Krüger and Yolken[22], who used ellipsometry to investigate the variation of the rate of growth of oxide films on the surface of iron with oxygen pressure. The shape of the curves shows that, even in a high vacuum, iron (and probably all metals except gold) have an oxide film on their surface. Numerous studies have shown that such thin oxide films are in fact present and constitute the main barrier to heterogeneous reactions. Perhaps the only optical method which makes it possible to measure the thickness of such thin oxide films without affecting the experimental conditions is the ellipsometric method.

The physical phenomenon which constitutes the basis of the ellipsometric method is that linearly polarised light incident on an absorbing surface becomes elliptically polarised after reflection from this surface. This method differs from those described above by the fact that measured quantities are not the change in light intensity at the angles, phase differences, and amplitude ratios of the lightwave components. The ellipsometric method is very

accurate in studies of film growth processes; according to Archer and Gobeli[23], the accuracy in the measurement of thickness reaches limits of 0.07 Å.

The method was first used to investigate the kinetics of the growth of oxides by Tronstad[24] and in the USSR elipsometry was used for similar purposes for the first time by Krylova[25], who measured the thickness of films on different metals. The ellipsometer was first applied to corrosion systems in the USSR by Andreeva[26, 27].

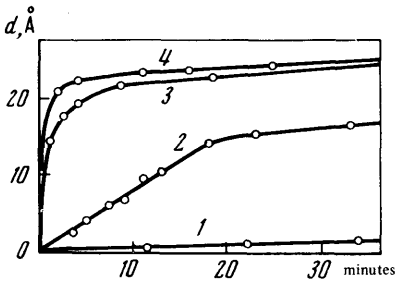


Figure 2. Variation of the thickness of the oxide film with time for iron in an atmosphere of oxygen[22] at different oxygen pressures (mmHg): *1*) 3.5×10^{-6}; *2*) 2.5×10^{-5}; *3*) 2×10^{-4}; *4*) 760.

The ellipsometric method makes it possible to measure also the refractive index of the oxide n. These measurements are simple if the film does not absorb light[28]. However, if the film does absorb light, the measurements of n must be made with a specimen immersed in liquids with different refractive indices[28]. For a fairly thick absorbing film (opaque film), the optical constants can also be determined using a single specimen.

Fig. 3 illustrates graphically the ellipsometric parameters, including the main parameters ψ and Δ.

Suppose that the incidence plane, perpendicular to the plane of the figure, forms a horizontal axis. The light incident on the specimen is initially polarised at an angle of 45° to this plane. The electric vector of the incident wave is 01 and that of the reflected wave is *OR* (Fig. 3). This picture corresponds to a dielectric specimen on which there are no surface films and the reflected light is linearly polarised. The ratio of the components of the *OR* vector corresponding to the polarisation in the incidence plane (r_p) and in the plane at right angles to it (r_s) defines the tangent of the ellipsometric parameter ψ:

$$\tan\psi = r_p/r_s \quad . \tag{6}$$

However, if there is a film on the surface of the support or the support is made of an absorbing material, the magnitude and directions of the r_p and r_s vectors will vary with time and the reflected light becomes elliptically polarised. The direction of rotation of the electric vector is indicated by arrows on the ellipses illustrated in Figs. 3*a* and 3*b*. The phase difference Δ for the r_p and r_s vectors constitutes the second ellipsometric parameter:

$$\Delta = \delta_p - \delta_s \quad , \tag{7}$$

where δ_p and δ_s are the phases of the r_p and r_s vectors respectively. Fig. 3 shows also two other ellipsometric parameters, λ and γ.

The exact theory relating the phase differences Δ to the thickness of the film is very complex; however, provided that the refractive indices of the film and the support are known, the ellipsometric measurements of the film thickness are greatly simplified. In this case it is possible to employ a linear approximation to the exact expressions relating Δ and the film thickness.

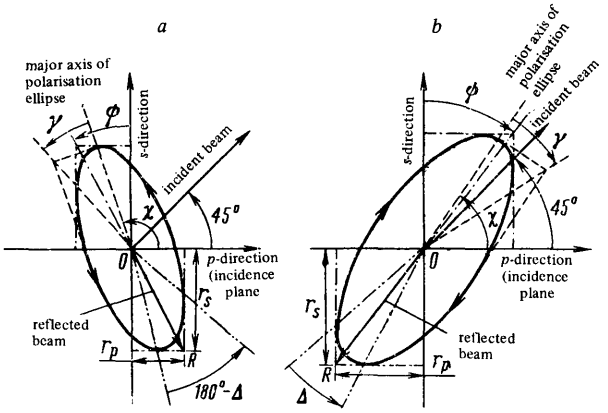


Figure 3. Graphical representation of different ellipsometric parameters: *a*) reflection at an angle of incidence smaller than the principal angle; *b*) reflection at an angle of incidence greater than the principal angle[29].

Starting with Tronstad[24], most investigators over a fairly long period employed Drude's linear approximation, which can be formulated as follows when the surrounding medium has a refractive index $n_2 > 1$:

$$\Delta - \bar{\Delta} = \frac{4\pi}{\lambda} \cdot \frac{\cos\theta \cdot \sin^2\theta \,(n_1^2 - n_2^2)}{(\cos^2\theta - n_2^2\alpha)^2 + n_2^4(\alpha')^2} \cdot [(\cos^2\theta - n_2^2\alpha) \cdot (n_1^{-2} - \alpha) + n_2^2(\alpha')^2] \cdot d \quad , \tag{8}$$

where Θ is the angle of incidence of the beam, n_1 the refractive index of the film, d the thickness of the film,

$$\alpha = \frac{1 - k^2}{\nu^2(1 + k^2)} \, , \quad \alpha' = \frac{2k}{\nu^2(1 + k^2)^2} \quad , \tag{9}$$

k the absorption coefficient of the metal, ν the refractive index of the metal, and λ the wavelength of the incident beam.

However, comparison of Drude's approximation with the exact theory shows that the error in the determination of the thickness using this approximation is very large and increases markedly with the thickness of the film. Comparison of curves *1* and *3* in Fig. 4, taken from Bennet and Bennet's review[29], shows this clearly. The figure also demonstrates that another linear approximation, proposed

by Archer, is much closer to the exact theory than Drude's approximation. Archer's approximation can be formulated as follows[30]:

$$\Delta - \bar{\Delta} = \frac{1}{[\cos^2\theta - a + \sin^2\theta\,(a^2 - a'^2)]^2 - (a')^2} \cdot \cdot [720\,(d/\lambda) \cdot \cos\theta \cdot \sin^2\theta\,(1 - n_1^2) \cdot \{(a - 1/n_1^2) \cdot \cdot [\cos^2\theta - a + \sin^2\theta\,(a^2 - a'^2)] - (a')^2\}] \quad , \tag{10}$$

where $\bar{\Delta}$ is the phase difference for a surface not coated by a film and $n = n' - jk$ is the complex refractive index of the support:

$$a = (n^2 - k^2)(n^2 + k^2)^2 \quad , \quad a' = 2nk/(n^2 + k^2)^2 \quad . \tag{11}$$

On the other hand, if the oxide film absorbs light, the use of approximate expressions for a non-absorbing film [Eqns. (8) and (10)] leads to serious errors in the simultaneous calculation of n_1 and d. This is indicated, in particular, by the experimental data of Chernykh and Yakovleva[31].

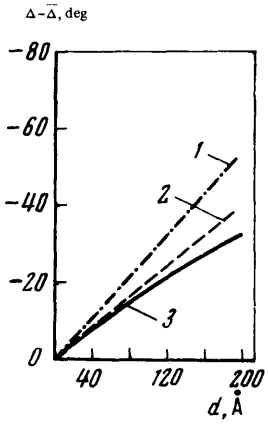


Figure 4. Comparison of Drude's (curve *1*) and Archer's (curve *2*) approximations with the exact theoretical relation (curve *3*). Data for alumina on the surface of aluminium[29].

However, there exist at least two methods, which make it possible to obviate these difficulties. The first involves the determination of the refractive index of the support and the film and of the refractive index of the film alone by independent methods, the ellipsometric method being used only to determine the film thickness in terms of Eqn. (10). Then, even if the film absorbs light, it is possible to obtain fairly accurate film thicknesses[32]. The second method, employed by Chernykh and Yakovleva[31, 33] and other investigators, does not require the experimental determinations of the refractive indices and of absorption by the film and support, but in this case difficulties of another kind arise. The method is based on the exact theory of the polarisation of light on reflection and hence requires fairly complicated calculations§. The results permit the plotting of nomograms taking into account the changes in n_1 and k. Analysis of the nomograms[31,33] shows that both ellipsometric parameters, Δ and ψ, depend very significantly on the changes in n_1, k and δ.

Experimental devices permitting the determination of the principal ellipsometric parameters ψ and Δ have been described in many original papers and reviews. One should note that the fundamental scheme of the measurements has changed little since the publication of the first studies by Tronstad. The following units are probably typical for any ellipsometric apparatus: emission collimator (source, slit, collimating lens), polariser, specimen with holder, compensator (quarter-wave plate), analyser, focussing lens, and detector.

Figs. 5 and 6 illustrate schematically two possible ellipsometric systems[29]. The recording can be both visual and photoelectric. Additional components, resembling half-shadow devices which increase the accuracy of visual readings[34,35] or Faraday cells which can be used for accurate photoelectric measurements of angular orientations (the accuracy with which the angles can be read is to within 1 second), can be built into ellipsometric systems similar to those shown in Figs. 5 and 6.[36] Moreover, gas lasers[37], mainly helium–neon lasers, have begun to be used recently as light sources in ellipsometers in order to increase the accuracy of the measurements.

A fairly advanced ellipsometer, a distinctive feature of which is its construction based on a commercial GS-5 goniometer produced in the USSR, was recently built at the Karpov Physicochemical Institute[38]. Four removable units, permitting its employment as an ellipsometer, were specially constructed for this instrument. The instrument has a photoelectric recording system.

Without considering in detail the extensive literature dealing with data obtained by measurements, we would like to quote here as an illustration several studies on the ellipsometry of thin films, which we believe to have a direct bearing on the corrosion-electrochemical behaviour of metals.

Bockris et al.[33] described experimental data obtained in an ellipsometric study of the surface of nickel in sulphuric acid solution. The nickel potential was maintained with the aid of a potentiostat. The observed dependence of the thickness of the oxide film on the electrode potential was of particular interest. However, the interpretation of the results aroused quite justified criticism[39]. The results of ellipsometric studies of the growth of oxide on nickel (in an alkaline medium) were published by Chernykh and Yakovleva[31,40]. They traced the relation between the change in the structure of the oxides and the change in the optical parameters; although some of the conclusions arrived at are controversial, on the whole these studies[31,40] are of great interest.

Goswami and Stachle[41] investigated the kinetics of the growth of passive films on iron and iron–chromium, iron–nickel, and iron–chromium–nickel alloys. The oxide films were formed on anodic polarisation of the electrodes in a borate buffer solution (pH 8.4). Their[41] results show that the dependence of the change in the thickness of the oxide on the potential is greater than would be expected for the inverse logarithmic law. The optical constants of the alloys not coated by oxidates are very close. The growth of films on the electrode surface leads to significant changes of the optical constants. For the same potentials, the film thicknesses on the iron and alloy electrodes are approximately the same. Thus one may suppose that in this case, the rate of the reactions at the electrode–electrolyte interface is determined by the electrophysical parameters of the oxide film and not its thickness.

§ These are simplified when electronic computer techniques are resorted to.

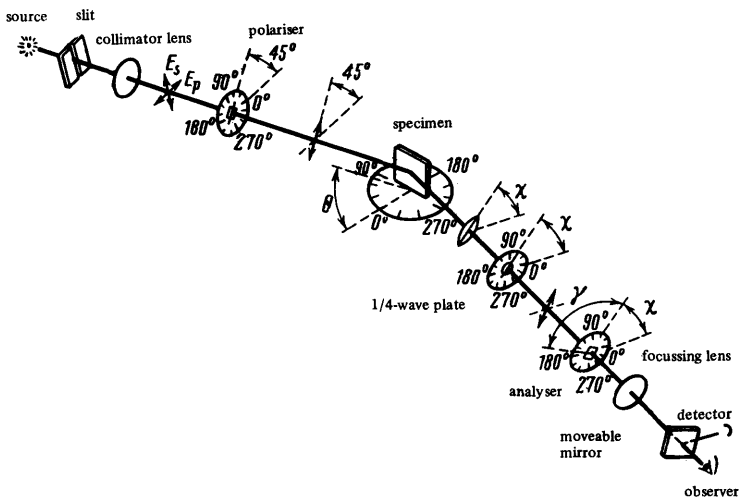


Figure 5. Ellipsometric system for the measurement of Δ and ψ for a 45° orientation of the polariser.

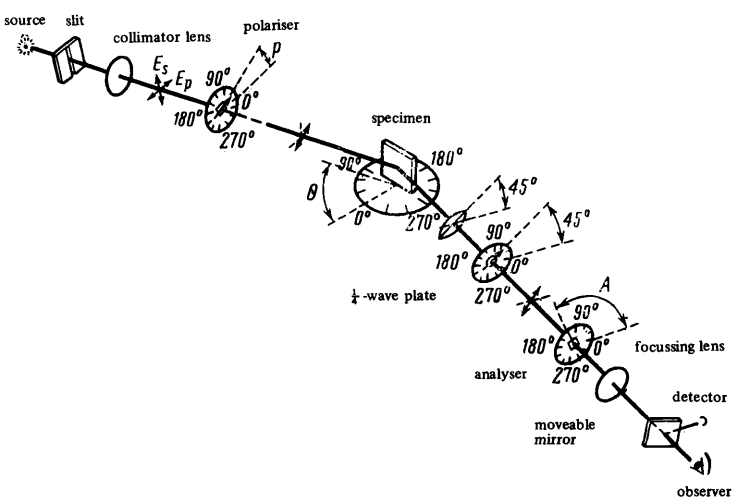


Figure 6. Ellipsometric system with a quarter-wave plate orientated at an angle of 45° for the measurement of Δ and ψ.

A recently published paper by Bockris et al.[42] describes a very extensive study dealing with the mechanism of the passivation of iron in neutral solutions. It was carried out by ellipsometric and coulometric measurements. The part of the investigation describing the methods[42] is of particular interest, since the authors described in detail the technique of the ellipsometric studies. The measured[42] refractive and absorption coefficients of iron oxides agree satisfactorily with other data. The results of the experiments of Bockris et al.[42] led them to the conclusion that at potentials more negative than the passivation potential iron is coated by a film of the hydroxide $Fe(OH)_2$. Very close to the passivation potential, the oxide γ-Fe_2O_3 begins to grow and its molar content in the film increases as the electrode potential shifts towards positive values. A potential shift by 0.5 V leads to complete recrystallisation of the film as γ-Fe_2O_3. According to the authors, the passivation of iron is in fact related to the appearance of the γ-Fe_2O_3 film on the iron surface. A number of studies in which an absorption mechanism of the passivation of iron in neutral solutions was proposed have been criticised.

Two recent studies by Sato and Kudo[43,44] deal with the same problem, namely the passivity of iron in neutral solutions. The first report[43] describes ellipsometric studies on iron in borate solution. It was observed that the oxide film can be completely removed from the electrode surface by cathodic reduction. It is stated that the minimum thickness of the surface oxide on iron is 9 Å. The oxide film exists on the electrode surface also in the region of active dissolution. At potentials between -0.3 and +0.9 V (s.c.e.)

the film thickness increases linearly with potential until the attainment of a thickness of 50 Å. The evolution of oxygen at higher anodic potentials does not disrupt the film. The problem of the distribution of potential in the iron–oxide film–electrolyte system is discussed on the basis of the experimental data obtained. According to Sato and Kudo[43,44], in the passive region the main potential jump is localised in the oxide film. The oxide film, consisting of Fe_3O_4 or γ-Fe_2O_3, was represented[43,44] as a two layer-structure with an outer hydrated layer and an inner non-hydrated layer.

In conclusion of the section dealing with ellipsometric studies on the kinetics of the growth of oxide films on metallic electrodes in electrolytes, noting yet again the extreme importance of these investigations, we should like to make certain critical remarks concerning the interpretation of the results of ellipsometric measurements. For example, Bockris and coworkers[33,42] believe it possible to infer the electronic conductivity of the oxide film from changes in the measured absorption coefficient. This approach is probably not entirely correct. Indeed, it is readily seen that a change in absorption index at a specific wavelength can only indicate a change in the number of electronic transitions from the corresponding level located in the forbidden gap of the oxides¶ and hence a change in the population of this level. In order to relate the change in the population of the level to the change in conductivity, it is necessary to show that the level is at least partially ionised at room temperature and hence can participate in the change of the equilibrium conductivity of the oxide film.

Moreover, it follows from the most general considerations that the electric fields localised in the double layer or in the oxide film can affect the ellipsometric parameters. Nevertheless, these effects are not taken into account in the studies quoted above, although the distribution of potential throughout the system has been discussed[43,44]. However, studies have been published during the last few years in which the effect of electric fields on ellipsometric parameters was in fact used to investigate the structure of the double layer and adsorption on the surface of the electrode. The next section of the review deals with these investigations.

III. ELLIPSOMETRIC STUDIES ON ADSORPTION AT THE METAL–ELECTROLYTE INTERFACE

The first study dealing with certain aspects of the effect of the double layer on the optical properties of the metal–electrolyte interface in relation to ellipsometric measurements was made by Stedman[45]. He chose a simple model of the double layer, whose parameters could be described in accordance with Delahay's theory[46]. Stedman[45] examined the effect of the structure of the double layer on the optical constants of the metal both in the absence and in the presence of specific adsorption. Stedman[45] quotes data obtained for aqueous potassium chloride–mercury and aqueous sodium fluoride–mercury systems. The wavelength of the light in the ellipsometric measurements was 546 nm and its angle of incidence was 70°. The surface charge of the metallic electrode was calculated from the experimental capacitance and potential of the electrode.

¶ One should bear in mind that the width of the forbidden gap in the majority of oxides exceeds 3 eV, while the energy of the light quantum emitted by the light sources usually employed in ellipsometers is less than 3 eV.

Fig. 7, taken from Stedman's paper[45], presents the variation of the ellipsometric parameters Δ and ψ with the electrode charge q_M at different sodium fluoride concentrations in solution. The shape of the curves shows that Δ and ψ depend very markedly on the surface charge, the dependence increasing on dilution of the solution. Thus it was shown that Δ and ψ can vary not only when a new phase grows on the surface of the electrode but also when the surface becomes charged. Moreover, the author points out that the $\Delta - q_M$ and $\psi - q_M$ (Fig. 7) relations have an inflection corresponding to the absence of a surface charge. Possibly this interesting experimental finding will permit the development of a new method for the determination of the zero-charge potential. Stedman[47] considered these problems in greater detail: in particular, he considered separately the effect of the dense and diffuse components of the double layer.

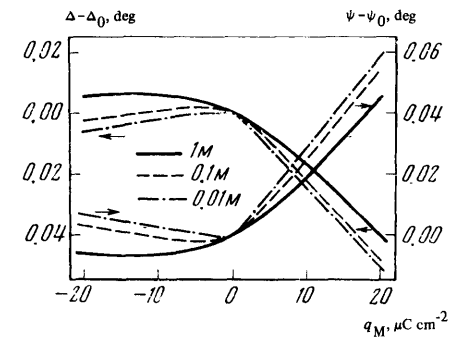


Figure 7. Variation of Δ and ψ with the surface charge of mercury in aqueous sodium fluoride; Δ_0 = 112.893, 113.125, and 113.145 and ψ_0 = 36.821, 36.831, and 36.832 for sodium fluoride concentrations of 1, 0.1, and 0.01 M respectively[45].

The Polish investigators Minc and Herbich[48] studied the influence of the double layer on the optical parameters of the metal–electrolyte interface[48]. They investigated ellipsometrically gold in 0.3 M sodium sulphate solution. To increase the sensitivity of this system, the reflecting element was made in the form of two plane-parallel gold plates between which light was repeatedly reflected. A distinct correlation was discovered between the rate of the electrochemical reactions and the "effective" reflection coefficient. The minima in the reflected light beam correspond to the minimum rates of the electrochemical reactions. Thus this study also confirms the possibility of employing ellipsometry for the investigation of the structure of the double layer.

The above problem was considered in two publications by Bockris and coworkers[49,50]. The first study[49] dealt with the ellipsometric investigation of the adsorption of anions at the solid–electrolyte interface. Silver, gold, rhodium, and nickel test electrodes were employed. The adsorption of Cl^-, Br^-, ClO_4^-, SO_4^{2-}, and OH^- ions was studied. The experimental apparatus consisted of a classical ellipsometer, but a differential recording system was employed. (A phototransistor, whose signal served as the reference signal, was introduced beyond the polariser, which made it possible to increase the sensitivity in the

measurement of the parameter Δ to within 0.002°.) The electrode potential was set by a potentiostat and was varied in 100 mV steps.

In the same study an attempt was made to relate the ellipsometric parameter Δ to the surface charge of the electrode. The authors endeavoured to allow for the electromodulation effect†, according to the interpretation of Hansen and Prostak[51]. Analysis of the equations quoted by Paik Woon-Kie et al.[49] convinced them that the changes in Δ are significantly related to the surface charge of the metallic electrode and depend very little on the charge distribution in the surface layer of the metal. The authors point out that, when the electromodulation effect is disregarded, a significant error may be made in the conversion of Δ into the amount of adsorbed substance. The main equation employed by the authors[49] is

$$\delta\alpha = \delta\Delta_{ads} \cdot (q -) + b\delta q_M \quad , \qquad (12)$$

where Δ_{ads} is the change in the parameter Δ on adsorption, q the amount of adsorbed anions in units of charge, b the electromodulation coefficient tabulated for different metals[49], and q_M the charge of the surface layer of the metal.

Fig. 8 (taken from Ref. 49) presents adsorption isotherms obtained on a gold electrode by the method described above. Similar isotherms were obtained on silver, nickel, and rhodium electrodes. The possibility of deriving such information demonstrates of course the extremely great value of the method.

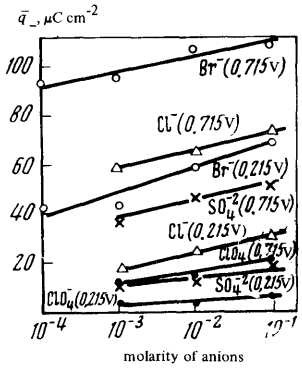


Figure 8. Adsorption isotherms of anions on a gold electrode obtained by ellipsometric measurements[49].

However, the authors themselves point out that the isotherms cannot be obtained in all cases. Thus the Δ–potential relations for the electrodes in hydroxide solutions is anomalous. The authors[49] explain this by the fact that the adsorption of even a monolayer of OH^- ions can (or should) be regarded as a new hydroxide or oxide phase. The fact that the authors[49] based their consideration of electromodulation effects on the model described by the theory of Hansen and Prostak[51] should also be noted. The reliability of the conclusions drawn from this theory is doubtful even as regards the very formulation of the problem of the mechanism of electroreflectance of metals. Moreover certain experimental data[52] disprove the fundamental conclusions of the theory[51]. We shall consider this problem in greater detail in the next section.

Paik Woon-Kie and Bockris[50] describe the results of a detailed experimental study of the joint influence of adsorption and electromodulation of the optical constants on the measured ellipsometric parameters. Although this investigation suffers from the same defects as the previous one, the experimental data and also the conclusions reached by the authors are extremely interesting.

They investigated[50] the variation of the ellipsometric parameter Δ for a gold electrode in 0.01 M NaBr in 0.001 N $HClO_4$‡ solution as a function of the wavelength. The light was made monochromatic using interference filters. The potential change from 0.11 to 0.61 V (s.c.e.). On the basis of the models described above, the authors attempted to calculate the contributions of the two effects — electromodulation and adsorption — and, having summed the two curves, to compare the resulting calculated curve with the experimental curve. A satisfactory agreement was obtained in the wavelength range from 4500 to 5500 Å; at higher wavelengths there was no agreement. The authors state[50] that characteristic contributions by the two effects probably occur for each metal.

One should note that so far experimental data have been obtained which definitely indicate that the change in the order on the electrode surface affects the fundamental ellipsometric parameters and ellipsometry can probably be used as an extremely sensitive method for the investigation of processes leading to such changes. However, so far there is no well-founded and clear theory which would allow a fairly clear-cut interpretation of the observed phenomena. This does not mean of course that studies in this field cannot be regarded as of very great value.

IV. SPECTROSCOPIC STUDIES IN THE ELECTRODE–ELECTROLYTE INTERFACE

The lack of spectroscopic studies on the electrode surface in electrochemical systems (until very recently) can probably be explained both by a number of technical difficulties and by the fact that the urgent need for such investigations arose quite late. Although the number of publications of spectroscopic data on electrodes is small, it is possible to discern a tendency for such investigations to employ the very latest advances in spectroscopy: multiple reflection and modulation methods.

The most promising spectroscopic methods, including those applicable to electrochemical systems, are related to the modulation of the intensity by some kind of external effect (for example an electric field). We then obtain a spectral distribution of the intensity of light reflected from the electrode surface differentiated with respect of this effect, i.e. instead of the I–λ relation, where I is the intensity and λ the wavelength of the light, we obtain the dI/dv–λ relation, where v is the external effect (for example a potential field or an electric field).

It is readily seen that the spectral distribution curves in a differential form have many advantages over the usual curves, primarily as a result of the sharp improvement of resolution. This aspect of the problem in relation to semiconductors and metals has been specially considered in two reviews[53,54]. The first study, dealing with the reflection spectra of metals modulated by an electric field applied in the electrolyte, was that of Feinleib[55], who obtained the electroreflectance spectra of gold and silver.

† The change in the optical constants of the metal when the electrode potential is altered.

‡ The Br^- ions were absorbed.

As regard method, the measurements of electroreflectance do not present fundamental difficulties but the measuring apparatus must be highly selective, since the signal/noise ratio at the input to the amplifier is usually small. A circuit for the measurements of electroreflectance and electroabsorption is presented in Fig. 9.

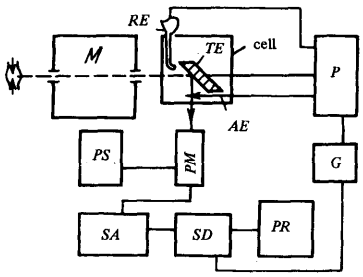


Figure 9. Circuit for the measurement of electroreflectance and electroabsorption in an electrode–electrolyte system.

Polychromatic light from the source passes through a monochromator (*M*) and falls on the surface of the electrode in the cell with the electrolyte §. The light reflected from the electrode falls on a radiation detector — a photomultiplier (PM). In addition to the test electrode (*TE*), the cell contains an auxiliary electrode (*AE*) and the reference electrode (*RE*) and is connected to a potentiostat (*P*). Moreover, a sinusoidal or pulsed alternating current from a generator (*G*) passes through the cell. This variable signal, which modulates the surface field of the electrode, also modulates the light reflected from the surface. Thus at the output from the photomultiplier there are two components of the potential: a constant component proportional to the overall flux reflected from the electrode (*R*) and a variable component proportional to the light flux modulated by the electric field (ΔR). As a rule the variable component is small — the degree of modulation is usually less than 1%. The variable signal at a fixed frequency is therefore amplified by a selective amplifier (*SA*) with a high amplification factor in a fairly narrow amplification band. After amplification the signal is detected synchronously (*SD*) and is recorded with a pen recorder (*PR*). A similar apparatus was described in detail by Akimov[56]. Different authors naturally describe somewhat modified experimental setups, but these modifications do not involve the fundamental and essential units enumerated above.

It is readily seen that the ratio $\Delta R/R$ is independent of the light source intensity spectrum and the light detector sensitivity spectrum but does depend on the changes in the optical and electrophysical (via the change in the local electric fields) properties of the electrode–electrolyte interface.

It was stated above that the electroreflectance effect on metals in an electrolyte was observed for the first time by Feinleib[55] and the mechanism of electroreflectance in this system was formulated by Hansen and Prostak[51], who suggested that the optical constants of the metal are modulated by the electric field owing to the modulation of the surface concentration of electrons (i.e. a change in the Fermi level on the surface of the metal). However, Lazorenko – Manevich and Stoyanovskaya[52], who compared their own data with the conclusions of Hansen and Prostak's theory[51], concluded on the basis of a comparison of the variation of electrode capacitance and electroreflectance with the potential of the gold electrode and the theory[51] cannot account for the mechanism of electroreflectance of metals. They[52] believe that not only the modulation of the surface concentration of electrons but also of their mobility may be the cause of electroreflectance. Incidentally, the value of their work[52] is by no means related to the critism of Hansen and Prostak's theory but is determined by their own experimental results. They obtained the variation of the electroreflectance from a metallic electrode with potential. They investigated gold, platinum, and silver electrodes and showed that the variation of the electrode potential may alter not only the intensity of the spectrum ($\Delta R/R$) but also its shape. In particular, a change in shape was observed in the oxidation of gold at a potential of about 1.5 V. Moreover, it was shown[52] that the shape of the electroreflectance spectrum of gold and silver changes significantly as a result of the specific adsorption of iodide ions from solution. They explained this phenomenon by the formation of chemical bonds between the iodide ion and the metal. The bond energy depends on the nature of the metal.

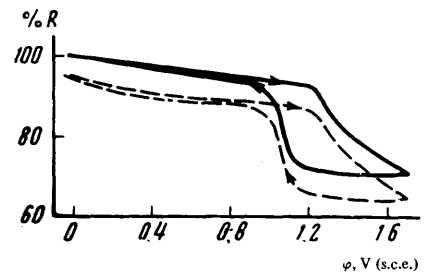


Figure 10. Measurement of the reflectance of gold in 1 *N* $HClO_4$ as a function of electrode potential. Continuous curve — in the absence of benzene; dashed curve — in the presence of benzene. Data for seven reflections are presented[57].

American investigators[57] studied the variation of the reflectance of gold under the conditions of a varying electrode potential. The main electrolyte employed was a solution of $HClO_4$. Single and multiple (sevenfold) reflection was used. The effect of adding benzene to $HClO_4$ on the variation of the reflectance with potential was examined. Fig. 10 shows the variation of the reflectance of the gold electrode with its potential in the presence and absence of benzene. The results[57] are fully consistent with those of Lazorenko – Manevich and Stoyanovskaya[52] in the sense that the variation of the potential changes not only the intensity but also the shape of the spectrum. Moreover, the

§ The requirements which must be met by the optical windows are of the usual kind for measurements of this type.

American workers[57] carried out an extremely useful analysis of the correlation between single and multiple reflection spectra. This relation may be described by the following equation:

$$(1/R)(\partial R/\partial E)_\lambda = (1/nI_n)(\partial I_n/\partial E)_\lambda \quad , \qquad (13)$$

where R is the reflectance of the electrode, $(\partial R/\partial E)\lambda$ a term related to the modulation of R by the applied field at a constant light wavelength λ, and I_n the light intensity after n reflections. It is understood that the shape and value of the (n/R) $(\partial R/\partial E)$–λ curves are independent of the number of reflections.

Mention should be made of the work of Barret and Parsons[58], who investigated the reflection spectra of a platinum electrode and the effect of the adsorption of ions of different substances (O_2, H_2, halogens, methanol, formaldehyde) on the optical constants of the electrode surface.

The data of McIntyre and Kolb[59], who investigated with the aid of reflection spectroscopy thin surface films formed on a metallic electrode, merits a more detailed consideration. They measured the $\Delta R/R$–φ (potential) and $\Delta R/R$–λ relations for platinum, gold and nickel under the conditions of anodic polarisation and the same relations for the adsorption of hydrogen and silver on platinum. Moreover, the results were used with the Kramers – Kronig dispersion relations to calculate the variation of the real and imaginary components of the dielectric constant with the energy of the light quantum. $\Delta R/R$ was calculated[59] as

$$\Delta R/R = [R(d) - R(0)]/R(0) = R(d)/R(0) - 1 \quad , \qquad (14)$$

where $R(d)$ is the reflectance of the metal–surface film–electrolyte three-phase system and $R(0)$ the reflectance of the metal–electrolyte interface. Measurements were made of the $\Delta R/R$–λ relations with light polarised parallel and at right angles to the plane of the electrode. These data permitted the calculation with the aid of equations quoted by McIntyre and Aspens[60] of both components of the dielectric constant of the surface phases. McIntyre and Kolb[59] employed a more complicated experimental apparatus than that used hitherto for analogous measurements. The more sophisticated apparatus permitted the measurement of the $\Delta R/R$ spectra up to 6.5 eV with a sensitivity of about 10^{-5} $\Delta R/R$ for a time constant of 1 s.

Having measured the $\Delta R/R$–φ and $\Delta R/R$–λ relations on platinum in 1 M $HClO_4$, McIntyre and Kolb[59] concluded that the oxide film on platinum consists of PtO (on the basis of the calculation of the absorption coefficient). Moreover, they found that the variation of the absorption coefficient of this layer, $\alpha = 4\pi k/\lambda = 2\pi\epsilon''/n_2\lambda$, has two maxima, the quantum energies of which are 3.4 ± 0.1 and 4.6 eV. At the maxima $\alpha = 5 \times 10^5$ cm^{-1}.

In spectroscopic studies of a gold electrode subjected to anodic polarisation in 1 M $HClO_4$ the authors observed that the oxide formed on gold at a potential of 1.6 V (n.h.e.) is Au_2O_3.

McIntyre and Kolb[59] quote data obtained in an optical study of the anodic oxidation of nickel in 0.1 M KOH. They made a detailed spectroscopic investigation of the surface oxide formed on the nickel electrode at a potential φ = 1.4 V (hydrogen electrode) and observed that the composition of the oxide is NiOOH. Fig. 11 presents curves relating the real (ϵ') and imaginary (ϵ'') components of the dielectric constant of the NiOOH film to the energy of the quantum calculated from the $\Delta R/R$ spectrum obtained for an electrode potential of 1.5 V (n.h.e.) in 0.1 M KOH. The ϵ' maxima corresponding to energies of 3.0 and 4.1 eV agree satisfactorily with data obtained by McClure[61] and Tippins[62] for the absorption of Ni^{3+} ions in corundum. A negative value of ϵ' is characteristic of the metallic conduction of this oxide phase.

The study of McIntyre and Kolb[59] lies at the boundary between spectroscopic investigations of the metal–electrolyte interface and investigations of metal–oxide–electrolyte systems. Below we shall consider studies dealing with systems of the latter type.

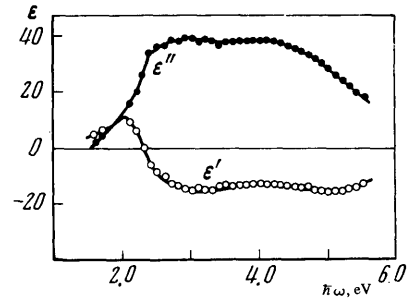


Figure 11. Spectra of real (ϵ') and imaginary (ϵ'') components of the dielectric constant of NiOOH; measurements made at a nickel potential of 1.5 V (s.c.e.)[59].

The paper of Holden and Ullman[63], describing the measurements of electroreflectance of oxidised tantalum and niobium, was published in 1969. An attempt was made to explain the mechanism of the generation of the electroreflectance signal by an interference effect arising in consequence of electrostriction in the oxide film. However, this view was criticised by Frova and Migliorato[64], who showed that the modulation of the interference bands by the electric field in the visible part of the spectrum, observed on tantalum oxide, must be accounted for by the modulation of the refractive index of the oxide. This conclusion was based on the very satisfactory agreement between the calculated and experimental data.

The present authors showed[65] that the spectrum of the light beam reflected from the surface of oxidised titanium and modulated by the field (we treat this effect as electroabsorption) can be interpreted only when the electroabsorption effect $-\Delta I/I$ can be attributed to modulation by the electric field of the optical constants of the surface oxide.

There are at present no theories of electroabsorption and electroreflectance in metal–oxide–electrolyte systems, but for a qualitative treatment one can probably assume that in a number of oxides arising on "rectifying metals" (titanium, tantalum, niobium, zirconium, tungsten, etc.) the mechanism of electroabsorption reduces to the "anomalous" Franz-Keldysh effect[66].

There are two possible research techniques based on electroabsorption in a metal–oxide–electrolyte system. In the first studies on the effect of the electric field on the position of the edge of the intrinsic absorption of crystals[67,68], it was shown that the position of the edge depends significantly on the magnitude of the applied field. This effect is entirely valid also for thin oxide layers formed on the surface of a metal, as shown in our investigation[65]. Thus it was natural to attempt the determination of the change in the electric field strength (potential jump in the oxide) as a function of the electrode potential by measuring the

change in the electroabsorption corresponding to the maximum on the electroabsorption–wavelength curve. The results of experiments of this kind have been published[65,69]. Fig. 12 presents $i-\varphi$, $C^{-1}-\varphi$, and $\Delta I/I-\varphi$ curves which we obtained[69] for a titanium electrode in 5 *N* KOH ¶. The data in Fig. 12 show that $\Delta I/I$ begins to increase on transition from active dissolution to passivation. The main growth of $\Delta I/I$ takes place in the region of passivation potentials. Since according to our data[65] the increase of $\Delta I/I$ is associated with the increase of the field in the oxide film, presumably the redistribution of the components of the overall jump in electrode potential takes place precisely in the region of passivation potentials. The potential jump in the oxide film increases not only as a result of the increase of the anodic potential but also as a result of the change in the location of the Helmholts potential jump, which leads ultimately to the inhibition of the dissolution of the metal. In the passive region the field strength in the oxide remains constant — $\Delta I/I$ is independent of the electrode potential. In the same range of potentials the surface oxide grows (the $C^{-1}-\varphi$ relation is linear). Hence it follows that the growth of the oxide is fully compensated by the increased potential jump in the oxide film due to the anodic potential shift.

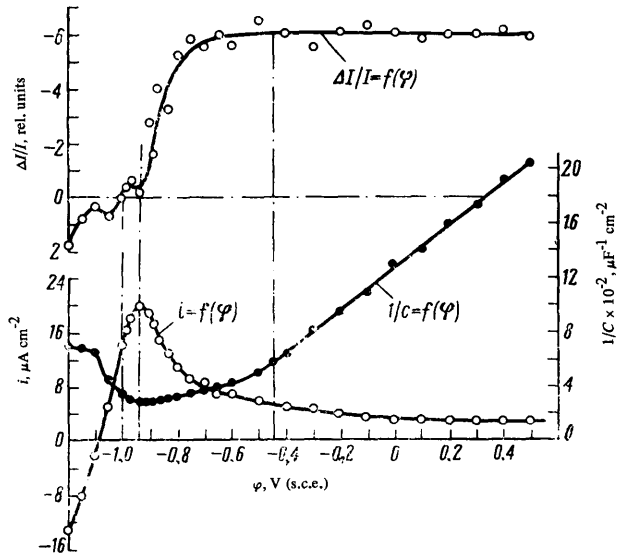


Figure 12. Variation of the current density i, the reciprocal of the capacitance C^{-1}, and the electroabsorption with the potential of a titanium electrode in 5 *N* KOH.

$\Delta I/I$ in a metal–oxide–electrolyte system also has a spectroscopic application. As already stated above, the electroabsorption spectrum has a maximum whose energy corresponds to the edge of the intrinsic absorption — the forbidden gap (ΔE_g) of the crystal. When the electroabsorption in a metal–oxide–electrolyte system is measured, the energy of the electroabsorption maximum on the electroabsorption–λ curve corresponds to ΔE_g for the oxide. Since ΔE_g is related to the main parameters of the oxide lattice, it follows that, having determined ΔE_g, it is often possible to identify the material of the oxide. Thus the maximum in the electroabsorption spectrum of the anodic oxide film on titanium[65] † agreed with ΔE_g for rutile single crystals measured by the same method[66].

The method of measurement of the electroabsorption spectra can probably be particularly useful in the study of structural transformations in surface oxides. Fig. 13 presents electroabsorption spectra which we obtained for a titanium electrode in 2 *N* H_2SO_4. The figure shows that the structure of the spectra changes significantly with the potential. Curves *1–3* (the passivation region) correspond fully to the rutile structure; however, on passing to potentials more positive than the total passivation potential, the absolute value of $\Delta I/I$ (curve with a maximum corresponding to an energy of 3.7 eV) begins to decrease (curves *4–6*) and a new short-wavelength $\Delta I/I$ maximum arises, its magnitude and energy depending on the electrode potential. Curves *7* and *8* corresponding to potentials of 0.2 and 0.5 V (s.c.e.), show that the energy of the new short-wavelength maximum is stabilised and assumes a value of 4.2 eV. We believe that the reason for the observed deformation of the electroabsorption spectra is that at more positive potentials the rutile structure may be replaced by the anatase structure, i.e. at potentials more positive than the passivation potential the rutile–anatase phase transition takes place in the oxide film on the titanium surface. It has been stated[70] that in many cases the anatase structure more readily gives nucleation.

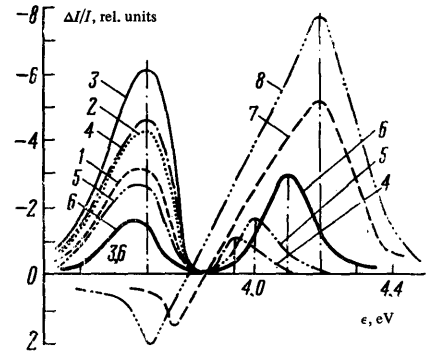


Figure 13. Electroabsorption spectrum obtained for the anodic polarisation of titanium in 2 *N* H_2SO_4 at different electrode potentials [V(s.c.e.)]: *1*) 0.45; *2*) 0.40; *3*) 0.35; *4*) 0.30; *5*) 0.25; *6*) 0.1; *7*) 0.2; *8*) 0.5.

The high sensitivity of the electroabsorption spectra to structural changes in the oxide may be demonstrated by the following example. Fig. 14 illustrates the electroabsorption spectra which we obtained from titanium–niobium alloys with different niobium contents. The measurements were made in 5 *N* KOH at a potential of 0.5 V. It is seen from the figure that the positions of the maxima in the electroabsorption spectrum depend significantly on

¶ Titanium is activated in this electrolyte and its surface oxide has the rutile structure over a wide range of potentials.

† We showed[11] that the oxide films obtained in the anodic polarisation of titanium in alkali have the rutile structure.

the niobium concentration in the alloy, which can be accounted for by the incorporation of impurity Nb^{5+} ions into the main TiO_2 oxide (rutile). Comparison of these data with the TiO_2–Nb_2O_5 phase diagram[71] suggests that the return of ΔE_g to a value characteristic of impurity-free rutile (3.7 eV), which occurs at a niobium concentration of 10%, can be explained by the fact that the initially homogeneous oxide becomes heterogeneous, since the new phase $TiO_2.Nb_2O_5$ appears. The appearance of this new phase can in fact promote the liberation of niobium from rutile.

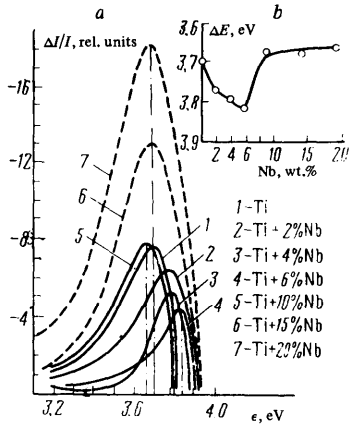


Figure 14. *a*) Electroabsorption spectra for titanium and titanium–niobium alloy electrodes obtained in 5 *N* KOH; *b*) variation of the energy of the electroabsorption maxima with niobium content in the alloys.

Gobrecht et al. [72] made a spectroscopic study of the surface of nickel under the conditions of anodic polarisation in 0.1 *N* sulphuric acid. They employed the electroreflectance method for this purpose and observed a change in the structure of the oxide in the range of potentials between primary and secondary passivation (0.8–1.3 V relative to the saturated calomel electrode). On the basis of a model which considered the inhomogeneity of the oxide film growing on the nickel surface, the authors explained the observed shift of the main absorption edge of the nickel oxide film with increased anodic potential by an increase of the concentration in the oxide film of nickel ions with a valence greater than two. The maximum rate of formation of these ions was observed at a potential of 0.97 V (s.c.e.). Thus, from an anodic potential of 0.76 V (s.c.e.), the outer layer of the oxide film is enriched in Ni^{3+} ions. This hypothesis of the authors is confirmed by a study of the variation of electroreflectance with the frequency of the modulating potential..

The data described above show that the application of various optical methods in the study of corrosion-electrochemical processes in an electrode–electrolyte system is extremely promising and may yield very valuable information about the mechanisms of these processes.

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