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PHOTOELECTROCHEMICAL PROCESSES ON ANODIC LAYERS

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Résumé. — Les propriétés semiconductrices des couches d’oxyde formées par oxydation anodique ou thermique de plusieurs alliages de fer avec le nickel et le chrome ont été déterminées en mesurant les photopotentiels et les photocourants relatifs aux systèmes Metal-Oxyde-Solution (de pH compris entre 2 et 11). Les résultats obtenus à pH 8,7 ont permis de classer les alliages en deux groupes, selon l’allure des signaux photoélectrochimiques obtenus. Le premier groupe comprend le fer, les alliages Fe-Cr, Fe-Ni avec une [Ni] < 40 % et les aciers des séries AISI 300 et 400 ; le second groupe comprend le nickel et les alliages Fe-Ni avec [Ni] > 40 %. Pour les alliages Fe-Ni avec une [Ni] > 40 % on a trouvé des différences entre les caractéristiques semiconductrices des oxydes obtenus anodiquement ou par voie thermique. Pour les aciers des séries AISI 300 et AISI 400 on a observé une différence de comportement quand le potentiel est compris entre 1100 mV (NHE) et 500 mV (NHE) lorsque le pH est inférieur à 4. On a étudié aussi l’influence de la densité de courant sur les caractéristiques des couches anodiques pendant leur formation.

Abstract. — Properties of anodic layers formed on various stainless steels and other iron base alloys were studied by means of photopotential and photocurrent measurements. The tests were carried out in borate buffer solutions and in sulphate solutions with pH ranging from 2 to 11. The study has been extended to layers formed by thermal oxidation in air. The results obtained at pH 8.7 indicated that the various materials can be grossly classified into two groups according to their photoelectrochemical behaviour : those behaving like Fe and those behaving like Ni. The first group comprises Fe-Cr alloys, Fe-Ni alloys below 40 % Ni, and all the examined stainless steels. To the second group belong Fe-Ni alloys with more than 40 % Ni. For Fe-Ni alloys with Ni > 40 % a difference of the semiconductor properties has been established between anodic and thermal oxides. A difference of behaviour was also observed between AISI 3xx type and AISI 4xx type steels in the electrode potential range 500-1100 mV (NHE) when the pH is below 4. Tests were also made in order to investigate the influence of anodic current density on the characteristics of anodic layers during their formation.

1. Introduction. — It is known since the early works by Becquerel [1] that when light is absorbed by an electrochemical system various phenomena occur, which can be detected by measuring the corresponding variations of the electrodic potential or of the current density.

If the primary absorption process of the radiation affects only the molecules present at the solid-electrolyte interphase, a simple electronic excitation of those molecules or a photochemical reaction may result [2-5]. In the first case together with fluorescence and phosphorescence phenomena an increase of the reactivity of the adsorbed species takes place, which can be accompanied with an exchange of electric charges between the adsorbent and the adsorbate ; this is particularly important when the solid is a semiconductor. In the second case the photochemical reaction leads to a concentration change for the species in the electrolyte solution, thus varying the existing redox equilibria.

When the solid phase is a metal, it was shown [6] that the absorption of the radiation can yield the photoemission of electrons, which hydrate and penetrate the solution for a few hundreds Å, where they can be captured by ions or other scavengers, or they can return to the metal. This phenomenon [7] depends on the energy of the incident photons, on the electrode potential, and scarcely on the nature of the metal.

When the electrode is a semiconductor [8], the radiation causes a change in the carriers population ; the minority carriers increase, and therefore, the rate of the reactions involving such carriers is highly modified : i. e. the rate of oxidation reactions increases when holes are the minority carriers, and the rate of reduction reactions increases when electrons are the minority carriers [9].

The vast amount of works on the electrochemical behaviour of semiconductors, and especially those on Ge and Si, led to the individuation of various photoelectrochemical processes, some photovoltaic regarding the solid state, other photogalvanic regarding the charge transfer at the semiconductor-electrolyte interphase.

The solid state processes occur in the region of the semiconductor (space-charge region) where electron-hole pairs generated by the incident radiation are separated by the electric field [9]. These processes should be very fast and should concern the metal-oxide junctions with barrier properties, the n-p junctions inversely polarized, and particularly the semi-
conductor surface where the space-charge equals the charge of the adsorbed ions and the electrolyte countercharge.

On the contrary, photogalvanic processes are characterized by a photodecomposition of the semiconductor [9, 10] leading to the formation of neutral species and ions in solution. These phenomena, due to the accumulation of holes in bounding orbitals or of electrons in non-bounding orbitals, involve ions migration through the semiconductor-electrolyte interphase; it is reasonable to assume that those processes are markedly slower than photovoltaic processes.

Recently semiconductor electrodes received particular attention for their possible application to the problem of solar energy conversion into chemical and electrical energy.

The study of the effects induced by light on electrochemical systems has a great importance also in the field of metal passivation and corrosion. Photo-effects measurements made on Ag [11], Ni [12], Cu [13] electrodes in the course of voltammetric cycles gave important contributions to the study of electrochemical reactions occurring at those electrodes and allowed the determination of the species corresponding to the various peaks of the voltammetric cycles. A common application of photopotential measurements has been the determination of the semiconducting type, n or p, of the layers formed on metals under different conditions. Studies are reported on Cu [13-24, 26, 44, 45] Cd [25, 26], Zn [26, 27], Ti [28-30], Ni [20, 31-33], W [34], Ag [1, 26, 35, 36], Co [37], Fe [19, 42], Zr [29, 38], Ta [39], Bi [40], Se [41]. Papers on some alloys are also reported: Cu-Ni [20], Fe-Ni [42], brass [1, 43, 44], and various steels [19, 45].

In the present work the properties of anodic layers formed on various stainless steels are studied by means of the analysis of photoelectrochemical responses. The study has been extended to layers formed by thermal oxidation in air.

2. Experimental. — Two kinds of experimental methods can be used in the study of photoelectrochemical phenomena: steady-state measuring techniques or dynamic techniques. An example of the first method is the comparison of stationary i(V) curves or of slow voltammetric cycles determined under illumination and in the dark. Analysis of photo-electric responses, that is the variation of photopotentials or photocurrents with time when the electrode is illuminated with single or repeated light pulses, belongs to the dynamic techniques.

The apparatus required for steady-state measurements includes standard electrochemical instrumentation, an electrolytic cell with a quartz window, and a high intensity light source. Dynamic measurements are performed by interposing between the light source and the cell a shutter for single pulses or a mechanical chopper for repeated pulses. It must be noted that tests with modulated light are necessary in the case of very low photopotential values (< 10 μV) in order to eliminate the background electric noise, what is achieved by means of a lock-in amplifier or of a box-car integrator. Figure 1 shows in schematic form the apparatus used for photopotential measurements; a similar circuit was used for photocurrents measurements.

![Block diagram of experimental setup](image)

**Fig. 1.** — Block diagram of experimental setup. 1. light source; 2. Chopper; 3. electrometer; 4. potentiostat-galvanostat; 5. lock-in amplifier; 6. box-car integrator; 7. recorder; 8. electrolytic cell.

3. Results. — In the present work the results obtained by studying the effects induced by light on different metal-oxide-electrolyte systems are reported. Various stainless steels and iron alloys, listed in table I, were tested after anodic passivation or air oxidation. The tests were performed in sulphate or in borate-buffer solutions in the pH range 2-11. The stainless steel electrodes were prepared from commercial materials, while the Fe-Ni and Fe-Cr alloys were expressly obtained by fusion of the metals under vacuum. The material structure was controlled by micrographic examination for every set of electrodes.

| Table 1 |
| List of materials tested |
| Commercial Stainless Steels |
| ASI 303 | ASI 410 |
| ASI 304 | ASI 416 |
| ASI 304L | ASI 420 |
| ASI 310 | ASI 430 |
| ASI 316 | ASI 430F |
| ASI 321 | ASI 431 |

Fe-Ni Alloys % Ni  
10 % - 15 % - 20 % - 44 % - 65 % - 90 %  
Fe-Cr Alloys % Cr  
4,4 % - 15 % - 24 % - 30 % - 42 %

The experimental tests can be divided as follows:

a) Photopopential measurements carried out at different electrode voltages during slow depolarizations of the anodes which were previously potentiostatically passivated for 30 min. Photopopentials were generated by single light pulses.
b) Photopotential measurements performed during
galvanostatic growth of the passive layers. These
tests were done both with single light pulses and with
modulated light (26 Hz). Cathodic polarisation at
50 μA/cm² for 30 min preceded the tests.
c) Comparison of voltammetric cycles (50 mV/s)
recorded under continuous illumination and without
illumination.

A set of experiments for each group was made on
electrodes oxidized in air at 300 °C.
Results obtained in borate-buffer solutions at
pH 8.7 with passivated electrodes can be divided into
two groups according to the photopotential response.
Stainless steels, Fe-Cr alloys, and Fe-Ni alloys with
Ni below 40 %, showed a photopotential response
similar to that obtained with Fe [42]. On the contrary,
the behaviour of Fe-Ni alloys with more than 40 % Ni,
was similar to that observed with Ni [42]. Figure 2
reports the photopotential responses for some of the
tested materials.

![Figure 2](image_url)

**FIG. 2.** Photopotential vs time response for various electrodes
anodically oxidized in borate-buffer solutions at pH 8.7. The
small numbers near the curves indicate the photopotential
value in mV.

In the case of alloys which show a behaviour simi-
lar to that of Fe, the photoeffects, at high anodic volt-
gages, consisted of one negative component having
a time constant of the order of ms. By decreasing
the anodic voltage, a second component appeared, posi-
tive in sign, whose amplitude increased with decreas-
ing electrode voltage. When the electrode potential
was lower than the oxygen reversible potential, the
amplitude of the positive component became larger
than the negative one, so that under stationary illu-
mination the total photoeffect appeared to be positive.
The tests showed that the phenomena observed by
setting on the illumination were symmetrically repro-
duced when light was switched off.

For the alloys having a behaviour similar to that of
pure Ni, the photoeffects consisted of one single nega-
tive component at high anodic voltages. By decreas-
ing the anodic voltage the photoeffects changed sign
and remained positive down to the hydrogen evolu-
tion potential. Figures 3 and 4 show the influence of
the electrode potential upon the photoeffects for
some of the electrodes tested. Figure 5 shows, for Fe-
Ni alloys, the electrode potential values, for which
a maximum of the photoelectric response was obser-
vied, versus Ni content ; in the same figure the electrode
potential values corresponding to photopotential
sign inversion are plotted.

In the case of air oxidized electrodes, photopoten-
tials are many times larger than for the anodically
oxidized electrodes but their trend is always similar to that obtained with anodically oxidized Fe. Positive photopotentials were observed only with pure Ni.

Both for anodically oxidized and for air oxidized electrodes the appearance of anodic photocurrents in the oxygen evolution potential region was observed by tracing voltammetric cycles with and without illumination. The photocurrent values were large for the alloys behaving like Fe, while for the other alloys the photocurrents were hardly detectable. Figure 6 shows the voltametric cycles determined on AISI 304 steel and on Fe-40% Ni alloy oxidized in air at 300 °C for 20 min.

Photopotential measurements during depolarizations of passive anodes in sulphate solutions at various pHs gave no sign change of the photoelectric responses for AISI 4xx steels, for Fe-Cr alloys, and for Ni-Ni alloys. On the contrary, a sign change was observed on AISI 3xx steels for pH values below 4. Figure 7 reports some of the observed curves.

Table II summarizes the results obtained by measuring with a lock-in amplifier the photopotentials generated by modulated light. The measurements were taken in the course of galvanostatic passivation. In table II the maximum photopotential values are related to the values of the slopes $\partial V/\partial Q$ of the voltage-charge curves determined during the galvanostatic layer formation. Figure 8 shows some of the recorded curves.

A marked difference of behaviour can be noted between AISI 4xx and AISI 3xx stainless steels. For the latter photopotentials increase with increasing anodic current density, while the slope $\partial V/\partial Q$ keeps almost constant.

For AISI 4xx steels the $\partial V/\partial Q$ values increase with current density and photopotentials markedly decrease. Single light pulse tests have shown that the photoeffects have always one single negative component.

Galvanostatic tests pointed out that light does not affect the kinetic laws for the layer formation. Instead, a marked influence of light on the reduction of the passive layers was sometimes observed during galvanostatic tests.
### Table II

Photopotential measurements during galvanostatic tests. Col. 1, material under study; col. 2, anodic current density; col. 3, slope of the voltage-charge curve; col. 4, maximum photopotential values; col. 5, electrode potential corresponding to photopotential maxima.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Current density $i$ ($\mu$A/cm$^2$)</th>
<th>$\partial V/\partial Q$ (mV/mC.cm$^2$)</th>
<th>$E_{\text{ph} \text{max}}$ (mV)</th>
<th>$V_{E_{\text{ph} \text{max}}}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 303</td>
<td>26</td>
<td>168</td>
<td>37</td>
<td>5</td>
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<tr>
<td>AISI 304</td>
<td>65</td>
<td>163</td>
<td>50</td>
<td>18</td>
</tr>
<tr>
<td>AISI 310</td>
<td>38</td>
<td>167</td>
<td>19</td>
<td>18</td>
</tr>
<tr>
<td>AISI 316</td>
<td>88</td>
<td>160</td>
<td>23</td>
<td>24</td>
</tr>
<tr>
<td>AISI 321</td>
<td>25</td>
<td>130</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>AISI 410</td>
<td>60</td>
<td>124</td>
<td>17</td>
<td>27</td>
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<td>8</td>
</tr>
<tr>
<td>AISI 420</td>
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<td>175</td>
<td>23</td>
<td>18</td>
</tr>
<tr>
<td>AISI 430</td>
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<td>160</td>
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<td>8</td>
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<tr>
<td>AISI 430F</td>
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<td>174</td>
<td>21</td>
<td>19</td>
</tr>
<tr>
<td>AISI 431</td>
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<td>56</td>
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</tr>
<tr>
<td>AISI 431</td>
<td>88</td>
<td>134</td>
<td>67</td>
<td>82</td>
</tr>
</tbody>
</table>

**Fig. 8.** - Electrode potential (a) and photopotentials (b) vs amount of passed charge during anodic layers formation at constant current.

**Fig. 9.** - Log. of photopotential values vs energy of the incident radiation for different materials. On Ni and on Fe the oxide layers were formed anodically, on AISI 304 steel the layers were formed by thermal oxidation.
As far as light wave-length influence is concerned, we always found that photoeffects begin to appear at a wave-length corresponding to an energy value of about 2 eV, independently of the materials and of the oxide formation procedure, figure 9.

4. Discussion. — Results of photopotential measurements on electrodes galvanostatically passivated in borate-buffer solutions, have shown that always when the electrode potential is greater than the oxygen reversible potential, a light pulse causes the appearance of a photopotential consisting of one single negative component with a time constant of the order of 1 ms. Voltammetric cycles traced with and without illumination indicated that in the same electrode potential range, light induces anodic photocurrents.

For all the cases examined, with the exception of Fe-Ni alloys above 40% Ni, by decreasing the anodic voltage the photopotential response with time is modified by the appearance of a second component which is slower than the first one and has a positive sign. The amplitude of such component increases by continuing to reduce the electrode potential and for a particular electrode potential exceeds the negative one. When this occurs, photopotentials, under continuous illumination appear to be positive. The electrode potential corresponding to the sign inversion is a little lower than the oxygen reversible potential.

Photoelectric responses to single light pulses contain a vast amount of information about the system. The trend of such responses sums up the modes according to which photoeffects are originated and disappear, and contains information on photovoltaic and photogalvanic phenomena. The interpretation of photoelectric responses is based on the possibility of distinguishing among the various effects producing the photopotentials. Referring to a simple model:

\[ \text{Metal/n-type semiconductor/p-type semiconductor/Electrolyte} \]

we tried to describe the photoelectric phenomena as indicated in figure 10, where imagined partial curves for two distinct processes (curves A and B) and the total curve \((A + B)\) are shown for various values of the ratio of the time constants for the two processes. It must be noted that the total photopotential trend strongly depends on the time constants ratio.

According to Gerischer assumption [9] referring to oxygen evolution reaction on semiconductor electrodes in the form:

\[ \text{H}_2\text{O} + 2 \text{h} = 2 \text{H}^+ + \frac{1}{2} \text{O}_2 \]

which involves electrons of the conduction band, we have as a logical consequence of our results that, with the exception of Fe-Ni alloys with Ni > 40% Ni, holes are the minority carriers at high anodic potentials. So, the Metal-Oxide-Electrolyte system behaves like an n-type semiconductor or like an inversely polarized n-p junction.

The faster photopotential component is due to the separation induced by light of electron-hole pairs within the electric field in the oxide layer. Holes accumulate on the electrolyte side while electrons go towards the metal. This causes a decrease of the electric field strength within the oxide, which is revealed on the external circuit as a negative photopotential. Steady-state is achieved when migration and diffusion currents due to minority carriers are equal. At constant voltage the increase of the minority carriers number causes an increase of the oxygen evolution rate. We made the reasonable assumption that the above described mechanism for photopotential generation must be valid in the whole range of electrode potential used, and that as a consequence the fast photopotential component is attributable to solid state processes.

The slow process, involving a flow of negative charges towards the solution, might be caused by photo-decomposition of the surface oxides according to the reaction:

\[ h\nu + \text{MeO}_x + \text{H}^+ = \text{MeO}_{x-1} + \text{OH}^- + 2 \text{h}. \]

Such interpretation is supported by the measurements performed during the formation of the anodic
oxides and by the influence of the electrolyte composition on the observed photoeffects. In this regard, we observed that during anodic oxidation the slow photopotential component is not present and that a change of the electrolyte composition mainly affects the slow component.

Moreover from the observation that the two photopotential components are present both when the illumination is switched on and when it is switched off, the fast component having almost the same amplitude in both cases, we imagined that the fast and slow processes occur in different regions of the layer. Thus we assumed that the layer behaves like an inversely polarized n-p junction, the n region being near the metal, where there is some reason to assume an excess of interstitial ions, and the p region being near the electrolyte, where the oxide structure is lacunar due to oxygen excess. However, for the extremely low values of the layer thickness, the situation pictured above must be thought in terms of a surface-charge inversion layer.

The assumption that two distinct processes concur to photo-potential generation, is consistent with the behaviour of AISI 3xx type steels for pH below 4, when an inversion in the photo-potential sign was observed. We thought that such inversion was due to an increase in the ratio of the time constants for the photovoltaic and photogalvanic processes. In fact we noted that by decreasing the pH, starting from pH 8.7, the time constant for the photogalvanic process markedly decreases. Of course a simultaneous increase in the time constant for the photovoltaic process should occur, probably due to structure differences of the anodic layers or to the layer thickness decreasing. In the first case the layer can retain water molecules or hydrogen ions in acid solutions, in the second case the small thickness values can produce an increase in the importance of tunneling effects, whose consequence is known to be that of increasing the time constant of photoelectric processes.

For Fe-Ni alloys with Ni > 40%, photopotential responses are different from those observed on the other materials. At high anodic voltages photopotentials, though negative, are markedly lower than those previously described and by decreasing the electrode voltage they change sign. For pure Ni the electrode potential corresponding to the sign inversion is very close to that reported by Rouse and Weininger [46] for the NiO flat-band potential. Figure 5 shows the variation of such potential with Ni content. For Fe-Ni alloys above 40% Ni, the behaviour of the Metal-Oxide-Electrolyte system is analogous to that of a p-type semiconductor, for which photopotentials are positive when the electrode potential is lower than the flat-band potential, and negative, but very small, for higher voltages.

The comparison of the anodically oxidized electrodes with those oxidized in air points out the influence of the oxide layer thickness on photopotential values. Photopotentials generally increase with increasing layer thickness. For Fe-Ni alloys with Ni > 40%, the comparison also shows the difference between the semiconducting characteristics of the anodic oxides and those of the air formed oxides: in this latter case photopotentials, with the exception of pure Ni, were always negative with a time response similar to that observed on anodically oxidized Fe. It must be noted that for AISI 310 stainless steel, which is known to be a material particularly resistant to high temperature corrosion, photopotentials were always smaller than for the other materials.

Referring to galvanostatic oxidation tests, the correlation between the slopes \( \partial V/\partial Q \) of the voltage-charge curves and photopotentials, table II, indicates a clear difference in behaviour between stainless steels of AISI 3xx type and those of AISI 4xx type. There is some reason to believe that \( \partial V/\partial Q \) is proportional to the electric field strength within the layer [47]. So when the \( \partial V/\partial Q \) values, i.e. the electric field strength, do not depend on current density, the explanation being that by increasing anodic current density also increases the number of mobile ions in the layer, then photopotentials increase with current density. For all the other cases, that is when the \( \partial V/\partial Q \) values change with current density, photopotentials decrease. This finding, together with the preceding observation about photoeffects generated on air oxidized Fe-Ni (Ni > 40%) alloys, shows that semiconducting characteristics of anodic oxides are greatly influenced by the number of mobile ions in the surface oxides.

Regarding the influence of the electrode voltage on photoeffects, on the basis of the previous discussion, we must conclude that the electrode potential values corresponding to photopotential maxima, have no relevant meaning because the maxima position should depend on the ratio of the photovoltaic and photogalvanic time constants.

Finally measurements carried out with different light wavelengths have shown that photoeffects begin to appear only when the energy of the incident radiation is greater than 2 eV, almost independently of the material composition. This is consistent with data reported by Kolb and McIntyre [48] for NiO and according to their interpretation we can suppose that charge generation processes are associated with electron transfer from 2p levels of the oxygen atoms to 3d or 4s levels of the metal.
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DISCUSSION


b) Les travaux de l'école soviétique du Pr. Rosenfeld et Oshe sur ce sujet sont de l'avis de ces auteurs, utilisés dans l'industrie soviétique, mais ils sont contestés par les théoriciens d'une autre école soviétique. Quelle est votre opinion sur la théorie de Rosenfeld au photopotentiel.

M. MAJA. — a) Tandis que le Pr. Trabaneli fait des mesures de photopotentiels pour étudier la corrosion des métaux nous faisons ces mesures surtout pour étudier les phénomènes de passivation.

b) Je crois que la théorie d'Oche et Rosenfeld ne tient pas compte de l'influence de la surface. Les phénomènes induits par la lumière intéressent surtout la surface des oxydes qui se forment pendant la passivation ont une épaisseur généralement inférieure à 100 Å, et alors met un faute toutes les théories qui se réfèrent seulement à la masse de l'oxyde.

M. FROMENT. — Finalement il apparaît qu'il n'y a pas d'évolution considérable des signaux de photopotentiels en fonction de la teneur des éléments majeurs (Fe, Ni, Cr) de vos alliages. Ne serait-il pas intéressant de se fixer sur un métal ou un alliage (nickel, alliage à
base de nickel) et d’y introduire des éléments mineurs comme le silicium. Ces éléments en faible concentration (~ 1 %) sont capables de modifier notablement les propriétés de conduction des courbes formées dans le domaine de passivité.

M. Maja. — C’est pour cela que j’ai étudié les alliages des séries AISI 400 et j’ai composé leur comportement par rapport à celui des alliages de Fe-Cr préparés dans mon laboratoire. Les alliages commerciaux contiennent des éléments mineurs que nous avons étudiés ; dans ce cas nous les avons étudiés sous influence sur les photo-effets. Peut-être que pour le Nickel les effets des éléments mineurs sont plus évidents.

M. Froelicher. — Professeur Maja connaissez-vous les travaux de Fratoni et Perone, car ces deux chercheurs interprètent les réponses photo-électro- niques en termes de variation de courant faradaïque au niveau de la double couche suivant un schéma équivalent de R. C. (identique à ceux utilisés dans la mesure des impédances électrochimiques).


M. Maja. — Je n’ai pas lu les travaux de Fratoni et Perone. Ce que vous m’avez dit me rend un peu perplexe parce que je ne crois pas que, en tous cas, on puisse faire un schéma équivalent de R. C. Par exemple, à pH 5,2 pour l’acier AISI 304 nous avons trouvé des courbes très complexes qui sont constituées par une première réponse négative suivie par une réponse positive, et suivie encore d’une réponse négative. En outre je pense que l’interprétation des résultats avec un schéma équivalent ajoute très peu à la connaissance physique des phénomènes.