Determination of the limiting current density through potential step measurements

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Processes such as anodic dissolution, prepassive film formation (salt and/or oxide, hydroxide film), and passive film formation are in the initial stage controlled by diffusion. Information about the value of the limiting current density ($i_l$) is needed for understanding the kinetics of passive film formation. In this study an alternative method, suitable for the determination of the $i_l$ through potential step measurements, is proposed. The method is based on the assumption that the reaction cannot proceed faster than that allowed by the $i_l$. In this case, the maximum reaction rate corresponds to the current density at the inflection point of the $i-t$ curve, and this current density is identified as the limiting current density. This method was used to determine the $i_l$ values of some Cr-13% stainless steels at five passive potentials in mixtures of 0.1 M H$_2$SO$_4$ + 0.1 M Na$_2$SO$_4$ with different pH values. The results for the limiting current density were compared with the corresponding $i_l$ values obtained from the diffusion overvoltage equation. The agreement between the two methods is satisfactory.

The importance of stainless steels as corrosion resistant alloys cannot be overemphasised. They are used in important applications where it is not possible to prevent the corrosion of less expensive materials by coating. To achieve stable passivity, a certain current density is needed. The value of this current density depends on the alloy composition, and strongly on the electrolyte composition (pH, anion content). Number of important papers has been published on this subject.

In an important previous study Alkire and Hafele described the passivation of Fe in aqueous solutions of H$_2$SO$_4$, using the potential step method in a following manner. First, there is rapid metal dissolution which causes an increase in metal salt concentration near the corroding surface. Nucleation of an adherent salt film occurs, which then grows by continued precipitation from the supersaturated electrolyte and also by the continued anodic dissolution of the metal. Formation of the passive oxide layer occurs under the porous salt layer, where the current density within the pores is high enough to passivate the metal underneath. The salt film begins to dissolve with the corresponding current density into the electrolyte, eventually to disappear altogether, leaving only the passive oxide film on the metal surface. From galvanostatic transient method experiments Frank concluded that when the imposed current density is smaller than the dissolution current density, i.e. for $i_0 < i_l$, no passivation occurs. Hafele called $i_l$ the limiting current density; below this value of the current density the passivation time becomes infinite.

In the present study, the potential step method was used to obtain $i-t$ curves for some Cr-13% stainless steels in electrolytes of different pH values. Two different methods were used to extract the $i_l$ values from these experimental data. The first method is based on the diffusion overvoltage equation and has been applied before. In the second method, the $i_l$ values have been proposed to be determined from the inflection points of the $i-t$ curves.

Experimental Procedure

Cylindrically-shaped specimens with diameters of 16 mm and a thickness of 3 mm, were made from rods of Cr-13% stainless steels X4Cr13, X13Cr13 and X23Cr13, which were in the annealed condition. Compositions of test materials are shown in Table 1. Prior to each experiment, working electrodes were mechanically ground down to 600 grit SiC paper and finally polished, first with 9µ and then with 3µ diamonds pastes to near mirror quality. The test electrolyte solutions used in the experiments were mixtures of 0.1 M H$_2$SO$_4$ and 0.1 M Na$_2$SO$_4$, with pH values of 2.42, 2.85 and 3.31, respectively.

For the corrosion study a Green cell, a Potentiogalvanoscan (used as a Potentiostat) and a compatible PC were used. Test specimens, with an
exposed surface area of approximately 1 cm², were fixed in a polytetrafluorethylene (PTFE) holder as the working electrode. A saturated calomel electrode (SCE) was used as a reference electrode, and the counter electrode was made of Pt. The working electrode was kept at the potential of -0.7 V versus SCE for 3 min to reduce the oxide film, then for 1 min at open circuit potential (OCP) to obtain a reproducible initial state. After that the potential step measurements were performed, varying the potential from the OCP to passive value of -0.1 V, 0.0 V, 0.1 V, 0.2 V, and 0.3 V versus SCE, respectively. The experiments were carried out at 30.0 ± 0.1°C without deaeration of the electrolyte.

Results and Discussion
With the instantaneous application of a constant potential, or the so-called "potential step measurement", a time dependent curve \( i-t \) is obtained (Fig. 1). The situation is considered in which the rate of an electrode reaction is determined by diffusion. The diffusion overvoltage \( \eta_d \) is established when the supply of reactants at the electrode, or the removal of the reaction products, is the rate determining process. In this case the potential of the electrode with a flow current is given by the Nernst equation for the equilibrium potential \( E_0 \). In this equation, however, the concentrations of components directly at the surface must be used and not those in the interior of the electrolyte. The diffusion overvoltage is equal to the difference \( \eta_d = E'_0 - E_0 \) between the equilibrium potential \( E'_0 \) in the absence of current flow, and the equilibrium potential \( E_0 \) which forms during current flow as a result of the changed concentration \( c_j \) of component \( j \) at the surface. When only one component is considered, the diffusion overvoltage can be obtained from the following expression:

\[
\eta_d = \frac{RT}{nF} \ln \left| \frac{i}{i_d} \right|,
\]

where \( z \) is the electrochemical valence number and \( F \) is Faraday's constant. According to Eq. (1), a linear relationship exists between the diffusion overvoltage and the logarithm of the mean value of initial current density, as is shown, for example, in Fig. 2. By extrapolating the line to the equilibrium potential where \( \eta = 0 \), the limiting current density can be obtained. These results are denoted in Table 2 by \( i_d \) (Eq. 1).

In the present contribution, an alternative method is being suggested for determining \( i_d \) from the potential step measurements. The starting point of this analysis is Fick's first law and equality of the charge transfer flux with transport flux. The current density \( i \) is given by the relationship

\[
i = i_d
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Fig. 2—Logarithm of \( i \) as a function of diffusion overvoltage for X13Cr13 stainless steel in 0.1 M H\(_2\)SO\(_4\) + 0.1 M Na\(_2\)SO\(_4\); pH = 2.85, \( E_o = -0.65 \) V versus SCE.

\[
i = -z \cdot F \cdot D \cdot \left( \frac{\partial c}{\partial x} \right)_{x=0}
\]

where \( D \) is the diffusion coefficient, and \( \left( \frac{\partial c}{\partial x} \right)_{x=0} \) the concentration gradient at the surface, i.e. for \( x = 0 \). By differentiation of this expression with respect to time \( t \), the reaction rate \( v \) is obtained at the surface, i.e.

\[
\frac{\partial i}{\partial t} = -z \cdot F \cdot D \cdot \frac{\partial}{\partial x} \left( \frac{\partial c}{\partial t} \right)_{x=0}
\]

The reaction rate is limited by the concentration gradient in terms of the diffusion layer concept. The maximum rate of diffusion across the Nernst layer occurs when the gradient is steepest, which is when \( c_{x=0} = 0 \). This concentration gradient corresponds to the limiting current density, so \( \left( \frac{\partial v}{\partial t} \right)_{t=0} \) must be zero (maximum reaction rate) for \( i = i_d \). In other words, the limiting current density can be determined from the inflection point of the \( i-t \) curve: \( i_d \) is identified as the current density at the inflection point of this curve.

In Fig. 1 the current density is presented as a function of time and the inflection point is denoted by the full circle. The values of limiting current density, as obtained by numerical differentiation of the \( i - t \) curves, are given in Table 2. The results for X4Cr13, X13Cr13, and X23Cr13 stainless steels at five passive potentials and in electrolyte solutions of three different pH values are presented. It can be concluded from the results in Table 2 that the average \( i_d \) values as determined from the inflection point of the \( i-t \) curves, are in a reasonable agreement with those obtained from the diffusion overvoltage equation (Eq. 1). Therefore, the suggested new method should be suitable for determination of the limiting current density from potentiostatic measurements.

Table 2—Obtained values of the limiting current density \( i_d \) for stainless steels X4Cr13, X13Cr13 and X23Cr13 at five different passive potentials and at three different pH values of 2.42, 2.85 and 3.31 for aqueous solution of 0.1 M H\(_2\)SO\(_4\) and 0.1 M Na\(_2\)SO\(_4\). For comparison, the \( i_d \) values obtained from Eq. 1 are also shown (\( i_d(Eq.\ 1) \)).

<table>
<thead>
<tr>
<th>Material</th>
<th>pH Value</th>
<th>( E ) (V/SCE)</th>
<th>( i_d ) (mA/cm(^2))</th>
<th>( i_d ) (mA/cm(^2))</th>
<th>( i_d ) (mA/cm(^2))</th>
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<tr>
<td>X4Cr13</td>
<td>pH = 2.46</td>
<td>( i_d )</td>
<td>( i_d(Eq.\ 1) )</td>
<td>( i_d )</td>
<td>( i_d )</td>
</tr>
<tr>
<td>X13Cr13</td>
<td>pH = 2.47</td>
<td>( i_d )</td>
<td>( i_d(Eq.\ 1) )</td>
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</tr>
<tr>
<td>X23Cr13</td>
<td>pH = 2.42</td>
<td>( i_d )</td>
<td>( i_d(Eq.\ 1) )</td>
<td>( i_d )</td>
<td>( i_d )</td>
</tr>
</tbody>
</table>
Conclusion

Metal passivation, including the formation and disappearance of the salt film, is controlled during the early stage by diffusion. In this situation the limiting current density controls the reaction rate; the reaction cannot proceed faster than is permitted by $i_d$. In this paper an alternative method for the determination of $i_d$ is suggested. The limiting current density is determined from the inflection point of the $i-t$ curves: the value of the current density at this point corresponds to the limiting current density $i_d$. The method was applied to the $i-t$ curves obtained for Cr-13% stainless steels under various experimental conditions. The agreement between the $i_d$ values obtained by the 'inflection point' method and the corresponding $i_d$ values obtained from the diffusion overvoltage equation is fair.

Acknowledgement

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References


