ANODIC SOLUTION OF METALS AT HIGH CURRENT DENSITY. II

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It was shown in a previous paper [1] that in the potential region corresponding to activated dissolution of iron, the rate of the anodic process on the polarization curve at constant potential increases up to a defined limit (before passivation sets in) with an increase in the concentration of chloride anions in the solution. This was explained by assuming that the anions take part in the iron-ionization process. In the potential region corresponding to the dissolution of passive iron it was found that the dissolution rate decreased with an increase in the salt concentration and that a decisive role is played by the removal of the reaction products from the electrode surface, since their accumulation results in passivation.

The effect of the pH of a sodium chloride solution on the rate of electrochemical solution and on the passivation of the iron was considered in [2].

The studies were made by taking the potentiodynamic polarization curves (as described in [1]) and by observing the state of the electrode surface using a special microscope ($\times$ 85) during a slow change in potential to positive values. These observations showed that an iron electrode in a sodium chloride solution becomes covered with a film which is obviously a salt at approximately the moment at which passivation occurs. At the specified, fairly high current density, the rate of transition of the metal cations into the solution becomes so great that a supersaturated salt solution forms at the surface (with continuous stirring of the solution) and leads to the film formation. This film is destroyed at the potential corresponding to the beginning of oxygen deposition. The formation of the film at the electrode evidently results in an abrupt inhibition of convection at the anode surface and this inhibits the removal of the oxidation products of the metal and thus facilitates passivation and sets a limit to the solution current. The formation of the film also inhibits the access to the surface of the electrode of the activating anions participating in the process.

In [3-5] it was shown that ClO_4^- anions at defined potentials (φ_a) can activate an iron electrode. Our experiment (Fig. 1) showed that the principles regarding the solution of iron in neutral $NaClO_4$ solutions at potentials more positive than φ_a for iron are analogous to those which we found previously in [1] for the dissolution of anodically activated iron in sodium chloride solutions: with an increase from 1 to 4 in the $NaClO_4$ concentration (with a constant stirring rate), the value of the maximum (criterial current) decreases until the beginning of passivation (i_{cr}) of the anodically activated metal. An increase in the rotation rate of the disc electrode decreases the passivation limits and makes it possible to obtain higher rates of solution of the iron.*

In the region of anodic solution of an active iron electrode in neutral solutions of $NaClO_4$, which occurs at potentials approximately 1.7 V less positive than the solution by iron anodically activated ClO_4^- ions, stirring the solution is not found to have any marked effect either on the rate of solution or on the potential corresponding to the beginning of passivation. This evidently occurs because passivation, which slows

*We shall call the destruction of passivation due to an increase in convection in the presence of activating ions "convective depassivation."

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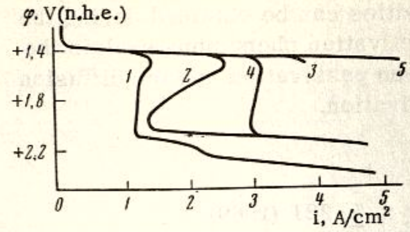

Fig. 1. Potentiodynamic polarization curves for an iron disc electrode: 1-3) stationary electrode; 4, 5) at 5000 rpm. Concentration of $NaClO_4$ solution, 1,4) 4; 2, 5) 2; 3) 1 N.

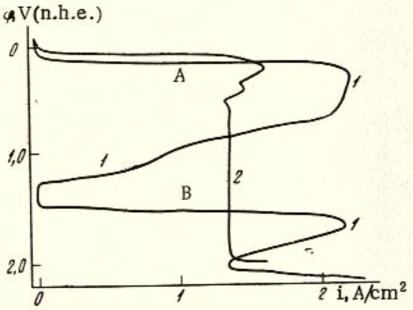

Fig. 2. Potentiodynamic anodic polarization curves for an iron electrode: 1) in 2 N $NaClO_4$ +0.2 N NaCl solution (A, activation by Cl^- ions; B, activation by ClO_4^- ions); 2) in 2 N NaCl solution.

down the solution of the active metal, is produced by the adsorption of oxygen on the surface of the electrode. The adsorption of oxygen occurs in this case at less positive potentials than the adsorption activation of iron by ClO_4^- anions [+1.4 V (n.h.e)] [4]. In this case the displacement, not only of the oxygen at the surface derived from its oxidation in air (as in the case of concentrated solutions of sodium chloride), but also of the oxygen adsorbed electrochemically at more positive potentials by the anions in the solution, is required for the anodic activation of the metal.

The passivation of an anodically activated metal by ClO_4^- ions begins with a small shift in potential from +1.4 V to the positive side (0.05 V), but at a current density many times greater than i_{cr} for an active solution (i.e., without the participation of salt anions). This value may be even further increased by an increase in the stirring rate of the solution, i.e., the passivation in this case is associated with concentration changes at the surface of the anode.

The activating effect of the anions appears at well-defined potentials, which depend on the nature of the dissolved metal, the nature and concentration of activating ions, and the temperature of the electrolyte. At other potentials these same anions may have a passivating effect. An example of this is shown by the experiments involving dissolution in electrolyte mixtures of NaCl and $NaClO_4$, since the potentials of the activation of iron by anions of these salts vary by more than 1 V. Depending on the concentration ratio $[Cl^-]/[ClO_4^-]$ in the solution, the ClO_4^- anions exhibit to a greater or smaller extent a passivating effect in the iron in a potential region which lies between the activation potentials for Cl^- and ClO_4 ions. With a sufficiently high ClO_4^- concentration the anode current in this region may be 1000 times less than the current in pure solutions of chloride (see the values of current density in the curves 1 and 2 in Fig. 2 at a potential of 1.3 V).* The passivating effect of the ClO_4^- ions may be explained by the fact that the adsorption of ClO_4^- increases more with a shift of the potential towards positive values than the adsorption of chloride ions and that the ClO_4^- ions in these specific conditions can displace chloride ions from the surface. (In an analogous way the adsorption of chloride ions on chromium is inhibited by the addition of sulfate or hydroxyl ions [6] to the solution.) At these potentials, however, the adsorbed ClO_4^- ions are no longer sufficiently deformed to produce anodic activation of the metal, and they therefore exhibit a passivating effect.

Measurements showed that the passivation of anodically activated iron in the presence of Br^- and I^- ions is due to the concentration changes at the electrode surface. When these anions are present in the solutions, the rotation of the disc electrode produces depassivation of the anode and makes it possible to obtain higher current densities.

In the region of potentials corresponding to dissolution of an active iron electrode in Na_2SO_4 and $NaNO_3$ as in $NaClO_4$ (before the activation potential), a very high rate of stirring does not increase i_{cr}, while an increase in the concentration of these anions does not lower the dissolution overvoltage, and consequently, no anodic activation effect is produced by the salt ions under these conditions. In solutions of the corresponding acids, the stirring produced some increase in i_{cr} but less than with anodic activation. The mechanism of the effect of stirring of the solution in the case of acids is clearly different and is associated with the removal of hydrogen ion concentration polarization.

*The value of i_{cr} in the case of the pure solution of sodium chloride is somewhat less than that in a mixed solution of NaCl and $NaClO_4$ (Fig. 2) due to the higher chloride ion concentration [1].

Thus, under conditions of anodic activation, very high current densities can be obtained during the electrochemical dissolution of metals. The peculiarities of the anodic activation phenomena explain the behavior we observed and, of greatest importance, the connection between passivation and the diffusion conditions at the electrode surface and the possibility of convective passivation.

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