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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Reduction of Vanadium from Alkaline Solutions

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Abstract—Effect of the potential sweep rate and temperature on the reduction kinetics of vanadate ions from alkaline solutions was studied. The nature of polarization in separate regions of the cathodic process was determined.

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The available published data [1, 2] indicate that vanadium(V) compounds in acid aqueous solutions can be successively electrochemically reduced to quadruple-, triple-, and double-charged states. All the reduction products are soluble and remain in the course of electrolysis in solution and impart to it blue, green, and violet coloration. It is difficult to recover vanadium from aqueous solutions because of the high negative potential of the last stage of reaction [3].

The reduction of vanadium in alkaline solutions is rather poorly understood, with the exception of results of [4], in which a low-concentration (0.05 M NaOH) alkali solution was used. It should be noted that there have been nearly no reports in the literature about studies of the nature of polarization in electroreduction of vanadate anions, although these studies are of indubitable interest for development of a technology for recovery of metals from industrial solutions.

Because of the importance of advances in this area, the aim of the present study was to examine the electrolytic reduction of vanadate ions from alkaline solutions.

EXPERIMENTAL

The kinetics and mechanism of vanadium reduction from alkaline solutions were studied using an electrolyte containing 0.0034 M NH_4VO_3 and 6 M NaOH.

The concentrations of vanadium(V) and alkali in this solution corresponded to the concentrations of industrial aluminate solutions from Gyandzha alumina plant, produced by the Bayer method [5].

The chemical composition of the solution under study, as regards the main components of the industrial solution, is as follows (g l^{-1}): Na_2O 186; Al_2O_3, SiO_2 0.40; SO_3 35, V_2O_5 0.30; P_2O_5 0.30; and other impurities.

Polarization curves were measured in the potentiodynamic mode with a P-5827 M potentiostat and N 307/1 recorder. A platinum wire with a surface area of 0.22 cm^2 served as the working electrode, and a platinum plate with a surface area substantially exceeding that of the working electrode, as the auxiliary electrode. A saturated silver chloride electrode served as reference.

As can be seen in Fig. 1 (curves *1*–*5*), the cathodic polarization curves show two portions of reduction of vanadate anions. This means that, in the reduction of vanadate ions, the process occurs in two stages. In portion I of the polarization curves at potentials of 0...0.60 V, vanadate ions are reduced to V(IV) ($V_2O_4 \cdot 2H_2O$). In portion II of the polarization curves at potentials of –0.750…–0.90 V, $V_2O_4 \cdot H_2O$ is reduced to V(III) ($V_2O_3 \cdot 3H_2O$).

It is known that salts of vanadic acid are the most stable vanadium compounds in alkaline media [6]. In electrolysis, V(V) anions (VO_4^{3-} and VO_3^-) are reduced to V(IV) and V(III) compounds [7, 8].

Cathode deposits were obtained from a solution of 6 M NaOH + 0.0034 M NH_4VO_3 by the potentiostatic method at potentials of –0.60 and –0.75 V. The deposits

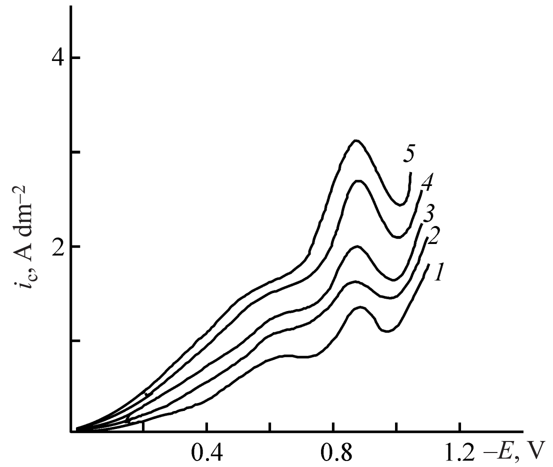

Fig. 1. Effect of the potential sweep rate on the electroreduction of vanadate ions. Solution composition 6 M NaOH + 0.0034 M NH_4VO_3. (i_c) Current density and (E) potential; the same for Fig. 3. Potential sweep rate (mV s^{-1}): (*1*) 10, (*2*) 20, (*3*) 40, (*4*) 60, and (*5*) 80.

were subjected to an X-ray diffraction analysis and it was found that their composition corresponds to the compounds $V_2O_4 \cdot 2H_2O$ and $V_2O_3 \cdot 3H_2O$.

The diffraction lines with interplanar spacings *d* 2.46, 6.42, 5.12 Å, found for the cathode slime obtained under the given conditions, correspond to characteristic reflections from hydrated vanadium oxide of composition $V_2O_4 \cdot 2H_2O$ [8].

Upon further shift of the cathode potential in the negative direction, a steep rise in the polarization curves is observed and hydrogen vigorously evolves by the reaction

$$2H_2O + 2e = H_2 + 2OH^-.$$

It can be seen in Fig. 1 that, as the potential sweep rate increases from 10 to 80 mV s^{-1}, the reduction process becomes 2.5 times faster. In addition, the rate of the cathodic process increases as the potential sweep rate grows in both portions of the polarization curves.

The data in Fig. 1 were used to plot the dependence of the peak current i_p on the square root of the potential sweep rate, $\sqrt{V}$. It is known [9] that such a dependence makes it possible to determine the nature of polarization in reduction of metals. As can be seen in Fig. 2, this dependence is linear in both portions I and II, which confirms the diffusion nature of the cathodic process in the vicinity of the maximum in the curves.

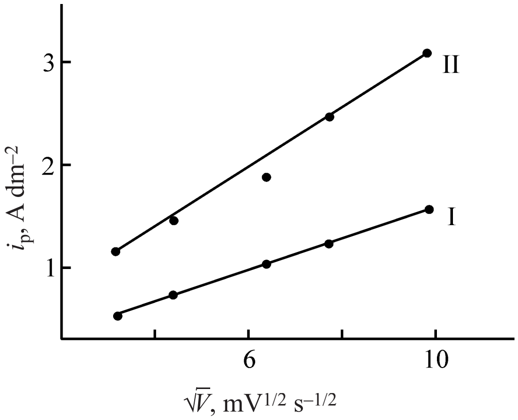

Fig. 2. i_p–$\sqrt{V}$ dependence for portions I and II.

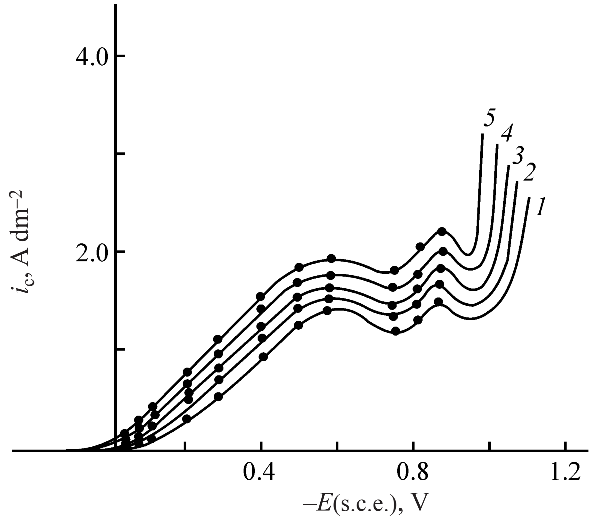

Fig. 3. Effect of temperature on the electroreduction rate of vanadate anions in solution of 6 M NOH + 0.0034 M NH_4VO_3. Potential sweep rate 10 mV s^{-1}. Temperature (°C): (*1*) 30, (*2*) 40, (*3*) 50, (*4*) 60, and (*5*) 70.

More detailed evidence about the nature of the cathodic polarization can also be obtained from data on how the rate of the electrode reaction depends on temperature. Therefore, the temperature dependence of the reduction rate of vanadate anions was studied. To elucidate the nature of the cathodic polarization in separate regions, the temperature-kinetic method was used [10].

A study of the temperature dependence of the rate of the cathodic process of reduction of vanadate ions demonstrated that this factor markedly accelerates the electrochemical reaction, i.e., an increase in the electrolyte temperature accelerates the electroreduction of the vanadate to different extents at different cathode potentials. As can be seen in Fig. 3, raising the temperature

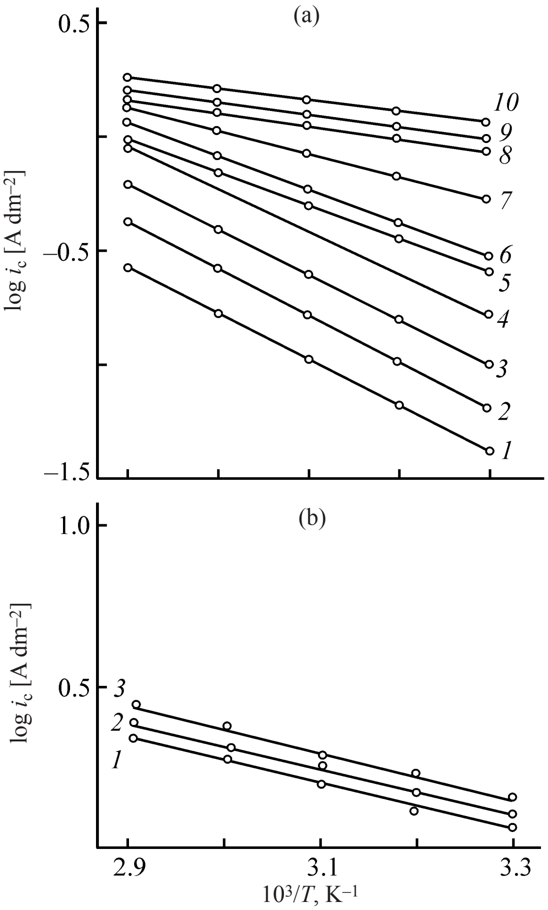

Fig. 4. log i_c–$1/T$ dependence at various potentials. Potential (V): (a) (*1*) 0.02, (*2*) 0.03, (*3*) 0.05, (*4*) 0.10, (*5*) 0.15, (*6*) 0.20, (*7*) 0.30, (*8*) 0.40, (*9*) 0.50, and (*10*) –0.60; (b) (*1*) 0.75, (*2*) 0.82, and (*3*) 0.90.

from 30 to 70°C leads to a 3.9-fold increase in the reaction rate at a cathode potential of –0.10 V. Upon a shift of the cathode potential in the negative direction, the influence of temperature becomes weaker. For example, the process becomes 1.22 times faster at a cathode potential of –0.60 V, and approximately 1.434 times faster at –0.90 V.

The graphical data in Fig. 3 were used to find the effective activation energy in regions I and II of the cathodic process. This was done using the equation

$$\log i_c = \text{const} - \frac{A_{\text{eff}}}{2.303RT},$$

where i_c is the current density; A_{eff}, effective activation energy; R, gas constant; and T, absolute temperature.

The activation energies were calculated from the slopes of straight lines plotted in the logic–$1/T$ coordinates.

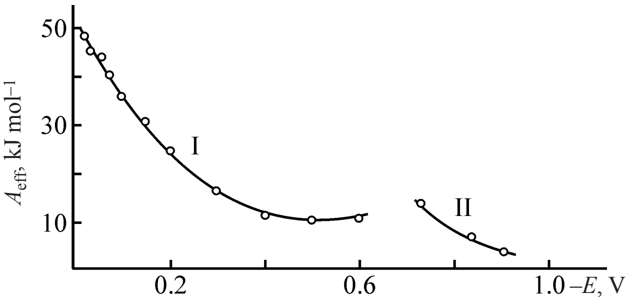

Fig. 5. Effective activation energy A_{eff} vs. the polarization potential E in a solution of 6 M NaOH + 0.0034 M NH_4VO_3 for portions I and II.

As can be seen in Fig. 4, the dependence of the rate of the electrode process on the inverse temperature is rather well expressed by straight lines with different slopes dependent on the cathode potential.

The data in Fig. 4 were used to calculate the effective activation energies A_{eff} of reduction of vanadate anions at various potentials, with the results obtained presented in Fig. 5.

It can be seen in Fig. 5 that, in portion I at potentials in the range –0.02...–0.60 V, A_{eff} reaches a value of 49.6 kJ mol^{-1}. As the cathodic polarization increases, A_{eff} rather sharply decreases to 11.2 kJ mol^{-1} at 0.40 V, and in portion II of the polarization curves at potentials of –0.75…–0.90 V, A_{eff} decreases from 14.2 to 4.45 kJ mol^{-1}.

Comparison of the data in Fig. 5 with published data [1] suggests that, in cathodic polarization, the process rate is controlled by the electrochemical polarization in the range –0.02…–0.10 V, and occurs under mixed kinetic control at –0.10…–0.40 V. In the range –0.40…–0.60 V, the cathodic process is limited by the concentration polarization. In portion II at potentials of –0.75…–0.90 V, the process also occurs in the concentration polarization region.

Thus, the temperature-kinetic data confirm conclusions based on results obtained in a study of the effect of the potential sweep rate on the cathodic process.

CONCLUSIONS

(1) It was found that, in reduction of vanadate anions from alkaline solutions, the process rate is controlled by the electrochemical polarization at low potentials of –0.02…–0.10 V, occurs under mixed kinetic control at –0.10…–0.6 V, and is limited by the concentration polarization at –0.75…–0.90 V.

(2) The experimental results obtained can be used to recover vanadium by the electrochemical method from industrial aluminate solutions.

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