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OXIDATION OF DIVALENT VANADIUM AT A GERMANIUM ANODE

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The kinetics of electrochemical reactions at a semiconductor electrode were first investigated by Brattain and Garrett (^1), who showed that the process of anodic dissolution of germanium proceeds by means of holes. In *n*-type germanium, holes are the minority charge carriers and their concentration is small; therefore, at a sufficiently positive potential, the rate of dissolution of electronic germanium is limited by the rate of diffusion of holes from the interior of the specimen, where their concentration is constant, to the germanium—electrolyte interface, where they enter into reaction. The occurrence of the process of anodic dissolution of germanium by means of holes was confirmed in a number of subsequent works (^{2}-4). Although in work (^1) only the process of anodic dissolution of germanium was studied, the authors considered it possible to extend their concept of occurrence by means of holes to all oxidative processes at a germanium electrode. However, the profound difference between the process of anodic dissolution of the electrode, in which the crystal lattice of the semiconductor participates, and the process of anodic oxidation of an ion present in solution, gives reason to doubt the correctness of such a generalization*. It was therefore of interest to study, from this point of view, some process of oxidation of an ion in solution at a germanium anode.

In the present work we investigated the oxidation of divalent vanadium ions on a rotating disk electrode made of single-crystal *n*-type germanium with a specific resistance of 1.8 ohm · cm and a diffusion length of 0.3 mm. A germanium disk 7.75 mm in diameter and 2 mm thick was mounted on a vertical axis, the side surface of the disk and the axis being insulated with a Teflon casing. The electrode was rotated by means of a synchronous electric motor through a pulley system; the rotation rate was measured with a stroboscopic tachometer.

The divalent vanadium solution was prepared by reduction of V_2O_5 in an H_2SO_4 solution with amalgamated zinc. Since V^{II} ions are rapidly oxidized by atmospheric oxygen, all measurements were carried out in an atmosphere of purified nitrogen.

The rate of oxidation of germanium does not depend on the intensity of stirring of the solution and, beginning at a potential of 0.5 V, is limited by the rate of diffusion of holes from the bulk of the specimen to its surface (“saturation current”) (^1). If divalent vanadium is introduced into the solution in which germanium dissolves at a potential more positive than 0.5 V, then the current flowing through the electrode at constant potential increases sharply; this increase ΔI is proportional to the concentration of V^{II} and to the square root of the angular rotation rate of the electrode ω, and may exceed by several times the “saturation current” of germanium dissolution (see Table 1).

* An analogous ambiguity also exists in the question of the source of electrons in reduction processes at a germanium electrode, as has been pointed out in the literature (^7).

Thus, V^{II} ions are freely oxidized at the germanium anode (with simultaneous dissolution of germanium) in the potential region in which the rate of dissolution of germanium itself (determined by the rate of diffusion of holes) reaches a limiting value. Under the conditions of this experiment, the rate of oxidation of V^{II} considerably exceeds the rate of diffusion of holes. Consequently, holes are not required for the process of oxidation of V^{II} at the germanium anode, i.e., the conclusion drawn in work (1) cannot be extended to all oxidative processes occurring at a semiconductor electrode.

Table 1

Potential, V	Current strength, mA before addition of V^{II}	Current strength, mA after addition of V^{II}	ΔI, mA
0.72	7.3	12.3	5.0
0.92	7.4	20.0	12.6
1.22	15.5	20.0	4.5

Since the oxidation of V^{II} at the germanium anode is always accompanied by dissolution of the germanium itself, to determine the rate of each of these two processes we used the previously described (5) method for separating processes that proceed simultaneously at a rotating disk electrode. The method is applicable in the case where the rate of one of the processes is proportional to $\sqrt{\omega}$, while the rate of the other does not depend on the intensity of stirring (in our case, respectively, the oxidation of V^{II} and the anodic dissolution of germanium). The total current density of these two processes at a constant value of the potential depends linearly on $\sqrt{\omega}$. Application of this method made it possible to separate the experimental curve obtained at the germanium anode in a solution of divalent vanadium (Fig. 1, 1) into two calculated curves: curve 2 for dissolution of germanium and curve 3 for oxidation of V^{II}.

Fig. 1. Polarization curves for the oxidation of divalent vanadium at a rotating disk germanium anode in a solution of 2.2 M H_2SO_4 + 0.9 M $ZnSO_4$ +

Fig. 1. Polarization curves for the oxidation of divalent vanadium at a rotating disk germanium anode in a solution of $2.2\ M\ H_2SO_4 + 0.9\ M\ ZnSO_4 + 0.067\ M\ VSO_4$. Electrode rotation rate 2550 rpm. 1 –experimental curve; 2 –calculated curve of anodic dissolution of germanium; 3 –calculated curve of oxidation of V^{II}.

Figure 1: Fig. 1. Polarization curves for the oxidation of divalent vanadium at a rotating disk germanium anode in a solution of $2.2\ M\ H_2SO_4 + 0.9\ M\ ZnSO_4 + 0.067\ M\ VSO_4$. Electrode rotation rate 2550 rpm. 1 –experimental curve; 2 –calculated curve of anodic dissolution of germanium; 3 –calculated curve of oxidation of V^{II}.

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As was shown by separate experiments, V^{II} ions are oxidized at a rotating disk platinum electrode to V^{III}, and the magnitude of the limiting current proved to be proportional to the concentration of V^{II} and to the square root of the angular rotation rate of the electrode, ω. As follows from the -

developed by V. G. Levich[6], the direct proportionality between the current and $\sqrt{\omega}$ indicates that the rate of oxidation of the ions is limited by the rate of their diffusion to the rotating disk electrode. It turned out that the limiting-current density in the case of curve 3 is equal to the limiting-current density for the oxidation of V^{II} on platinum. Consequently, the rate of oxidation of divalent vanadium at a germanium anode, as at a platinum anode, is determined by the rate of diffusion of V^{II} ions from the bulk of the solution to the electrode surface. Thus, the semiconducting character of the germanium anode has no effect on the kinetics of oxidation of divalent vanadium.

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