Thus, one can conclude from the experimental data discussed that there is a substantial change in the character of the SDOP as one goes from amorphous to crystalline TiO_2, but there is practically no change as one goes from anatase to the rutile modification. Differences in the position and shape of the curves of SDOP and in the values of photocurrent are due to differences in the structure of the electrode's SCR, to changes in the film's bulk conductivity, and to changes in the relative contributions of bulk and surface recombination.

LITERATURE CITED

1. J.-L. Desplat, J. Appl. Phys., 47, 5102 (1976).
2. H. Yoneyama, H. Sakamoto, and H. Tamura, Electrochim. Acta, 20, 341 (1975).
3. W. Gissler, P. L. Lensi, and S. Pizzini, J. Appl. Electrochem., 6, 9 (1976).
4. A. J. Nozik, Nature, 257, 383 (1975).
5. G. P. Shevchenko and V. V. Sviridov, in: Abstracts of Papers, First All-Union Conference on Silverless and Unconventional Photoprocesses [in Russian], Naukova Dumka, Kiev (1972), p. 186.
6. A. A. Krasnovskii and G. P. Brin, in: Molecular Photonics [in Russian], A. A. Krasnovskii and B. S. Neporent (editors), Nauka, Leningrad (1970), p. 161.
7. V. V. Sviridov, T. V. Gaevskaya, G. P. Shevchenko, N. I. Kuntsevich, G. A. Branitskii, M. I. Ivanovskaya, and G. A. Sokolik, Zh. Nauchn. Prikl. Fotog. Kinematogr., 20, 460 (1975).
8. V. V. Sviridov, G. P. Shevchenko, and T. I. Serdyuk, Zh. Nauchn. Prikl. Fotogr. Kinematogr., 21, 48 (1976).
9. G. L. McLeod, Photogr. Sci. Eng., 13, 93 (1969).
10. K. Nobe, G. L. Bauerle, and M. Braun, J. Appl. Electrochem., 7, 379 (1977).
11. K. L. Hardee and A. J. Bard, J. Electrochem. Soc., 122, 739 (1975).
12. L. A. Harris and R. H. Wilson, J. Electrochem. Soc., 123, 1010 (1976).
13. J. G. Mavroides, D. I. Tchernev, J. A. Kajalas, and D. F. Kolesar, Mater. Res. Bull., 10, 1023 (1975).
14. F. Möllers, H. J. Tolle, and R. Memming, J. Electrochem. Soc., 121, 1160 (1974).
15. A. I. Kulak, V. P. Pakhomov, V. V. Sviridov, and G. L. Shchukin, Élektrokhimiya, 15, 538 (1979).

KINETIC ISOTOPE EFFECT IN HYDROGEN EVOLUTION ON CHROMIUM, MANGANESE, AND IRON FROM ACIDIC SOLUTIONS

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It had been shown in the work of Kolotyrkin and co-workers [1-3] that the so-called chemical metal dissolution with hydrogen evolution is realized with chromium, manganese, and iron. The special feature of this process is independence of its rate from electrode potential. In the present work we measured the kinetic isotope effect (KIE) for protium and tritium in acidic solutions, both in hydrogen evolution due to chemical metal dissolution and during cathodic polarization of the metals, i.e., with the chemical and the electrochemical mechanism of hydrogen evolution. Previously we compared the KIE for these two mechanisms in hydrogen evolution from alkaline solutions on mercury [4] and mercury–gallium alloys [5].

The experimental procedure was basically the same as in [6]. All chemicals were at least twice redistilled or recrystallized. The solutions were prepared with twice-distilled water, and prior to the experiments they were cathodically polarized at platinized platinum for about 10 to 12 h with a current of about 10 mA while constantly passing hydrogen and stirring with a magnetic stirrer. The measurements were conducted at 30°C in 1 N H_2SO_4 solutions, and for manganese, in 0.1 and 0.36 N H_2SO_4. The values of potential reported below are stated relative to the normal hydrogen electrode. The error in the determination of the separation factor (S) was not over 5%.

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We used vacuum-smelted iron (purity 99.94%) and two chromium samples: Cr(1) was chromium smelted in vacuum (purity 99.98%); Cr(2) was obtained electrolytically from sulfuric acid solutions and then refined (purity 99.84%). Prior to the experiments the surfaces of chromium and iron were cleaned with emery paper, then with glass powder, and washed in succession with heptane, alcohol with alkali, and twice distilled water. Manganese was deposited electrolytically on a platinum substrate from ammonium sulfate solutions with the method of [7]. The purity of the metal sample thus obtained was 99.99%. After manganese deposition the electrode was washed with twice distilled water and transferred – with the shortest possible time of contact with the air – to the measuring cell which was purged with a strong flow of hydrogen. Then the electrode was brought in contact with the solution while polarized.

The chemical dissolution rates of the metals examined were determined in our experiments from the amount of hydrogen evolved. Including the corrections for temperature and solution composition, the values obtained are in harmony with literature data [1, 2, 8, 9]. Also in harmony with literature data are the steady-state potentials, φ_{SS}, observed by us for Cr(1), Mn, and Fe [1-3, 8-10]. For manganese, φ_{SS} is shifting in the positive direction with time (the rate of potential change was about 0.1 V/h.*) The φ_{SS}-value for Cr(2) is 0.1 V more positive than that for Cr(1), viz., −0.4 V.

The parameters of the polarization curves of cathodic hydrogen evolution obtained in our experiments are in harmony with literature data; for Cr(1), the slope of the Tafel line is 100 to 110 mV, and φ for a current of 10^{-2} A/cm^2 is −0.61 V, which is close to the data of [8, 11]. For Cr(2), the slope is the same but the overpotential (η) is 100 mV lower. For iron, the parameters of the polarization curves are in good agreement with the data of [3, 10]. Polarization of the manganese electrode with currents up to 0.7 A/cm^2 in 0.1 N H_2SO_4 does not lead to any change in electrode potential; this remains at φ_{SS}. A similar effect was observed for acidic solutions in [12].

Polarization curves obtained in our experiments are given in Fig. 1. Curves 1 and 2 are the cathodic curves for hydrogen evolution at the start of the experiment, curves 1' and 2' are those at the end of the experiment (after 5 h of work).† The vertical dashed lines show the rates of chemical metal dissolution [A for Cr(1), B for Fe]. For Cr(1) at a potential of −0.71 V, the rate of hydrogen evolution by the electrochemical mechanism is an order of magnitude higher than the rate of the chemical mechanism; hence the value of S measured at this potential is determined practically only by the electrochemical mechanism. At potentials more positive than φ_{SS}, tothe contrary, hydrogen evolution only occurs by chemical dissolution of the metal, and S is determined by the chemical mechanism of hydrogen evolution. One can see from Fig. 1 (curve 1) that on Cr in the absence of an external current, i.e., at φ_{SS} = −0.51 V, hydrogen evolution to 80% is due to chemical dissolution of the metal, and only to 20% to the electrochemical mechanism. For iron (curve 2) in the absence of an external current, hydrogen evolution is due in equal measure to the chemical and the electrochemical mechanism, and in this case we have some "mixed" separation factor. At sufficiently high cathodic potentials, the rate of hydrogen evolution via the electrochemical mechanism on iron is more than two orders of magnitude higher than the chemical current. Thus, in this region we measured a value of S arising from the electrochemical mechanism alone.

Figure 2 shows S as a function of φ. One can see from this figure that for iron and chromium, S remains constant within the experimental error limits over a wide range of potentials. The time shift of the cathodic polarization curve to more positive potentials which is found for chromium and iron does not lead to changes in S over the first 8 h of work. But for iron, longer contact with the solution is attended by a decrease in the separation factor (without any further decrease in overpotential). The data for iron are presented as the two plots c and c' in Fig. 2. The first plot reflects the results of measurements during the first 8 h, the plot c' was obtained when the electrode had been in contact with the solution for 30 h. The isotope effect measured by us at manganese in the absence of an external current, i.e., when hydrogen evolution is due to chemical dissolution of the metal, was 12.7 ± 0.7; at current densities which are an order of magnitude higher than the chemical dissolution current, S = 12.4 ± 0.6.

The value of S is found to remain constant over a wide range of potentials for iron and chromium. Moreover, at all three metals investigated, S does not change when hydrogen evolution changes from the chemical to the electrochemical mechanism. It had been shown in [13, 14] that the KIE depends on the multistep mech-

*With manganese, one experiment lasted about 20 min.

†The principal decrease in potential occurs during the first three to four hours of work. The anodic branch of the polarization curve does not shift in time.

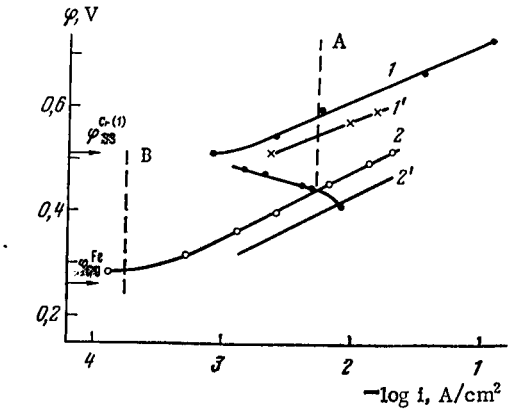

Fig. 1

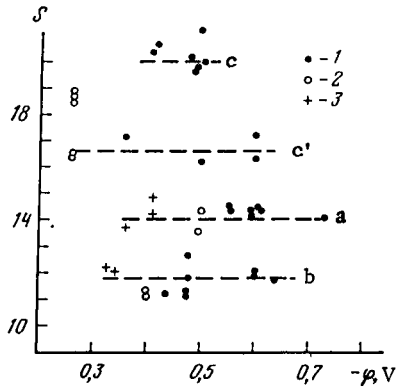

Fig. 2

Fig. 1. Cathodic polarization curves of hydrogen evolution from 1 N H_2SO_4 solutions: 1 and 1') Cr(1), 2 and 2') Fe (explanations in the text); 1") the anodic polarization curve measured at Cr(1).

Fig. 2. The protium–tritium isotope effect (S) as a function of φ: a) Cr(1); b) Cr(2); c and c') Fe. 1) $\varphi < \varphi_{ss}$; 2) $\varphi = \varphi_{ss}$; and 3) $\varphi > \varphi_{ss}$.

anism of the hydrogen evolution reaction. One can suggest, of course, that the isotope effects are the same in the two different hydrogen evolution mechanisms for purely accidental reasons. However, it would then be necessary in explaining the experimental data to suggest that the KIE also has the same dependence on the nature of the metal for the two different mechanisms, and this is unlikely. It is more realistic to suggest that the mechanisms of the elementary act of hydrogen are the same for the chemical and the electrochemical mechanism of hydrogen evolution. The metals examined have a number of common properties: the possibility that the chemical dissolution mechanism is realized at them, constancy of the KIE as one goes from the chemical to the electrochemical mechanism, and independence of the KIE from electrode potential. One can suggest on this basis that the mechanisms of hydrogen evolution are the same on these metals. One can see from Fig. 2 that the absolute values of S depend on the nature of the metal. In terms of a single mechanism of hydrogen evolution, a dependence of the isotope effect on the nature of the metal can be explained, either by a difference in the proton bond energies in intermediates or by a difference in the proton jump distances [15].

LITERATURE CITED

1. Ya. M. Kolotyrkin and G. M. Florianovich, Zashch. Met., 1, 7 (1965).
2. Ya. M. Kolotyrkin and T. R. Agladze, Zashch. Met., 3, 411 (1967); 4, 721 (1968).
3. G. M. Florianovich, Ya. M. Kolotyrkin, and L. A. Sokolova, in: Proceedings of the Third International Congress on Metallic Corrosion, Vol. 1 [in Russian], Mir, Moscow (1968), p. 196 [English edition: Mir, Moscow (1969)].
4. V. M. Tsionskii and V. L. Krasikov, Élektrokhimiya, 12, 961 (1976).
5. T. Sh. Korkashvili, V. M. Tsionskii, and L. I. Krishtalik, Elektrokhimiya, 14, 975 (1978).
6. V. M. Tsionskii and L. I. Krishtalik, Élektrokhimiya, 5, 1184 (1969).
7. N. T. Gofman, R. I. Agladze, Sh. I. Tsertsvadze, A. K. Chkoniya, and É. V. Kabzinadze, in: Electrochemistry of Manganese, Vol. 3 [in Russian], Metsniereba, Tbilisi (1967), p. 155.
8. Ya. V. Durdin, L. Kish, and V. I. Kravtsov, in: Proceedings of the Fourth Conference on Electrochemistry [in Russian], Academy of Sciences of the USSR, Moscow (1959), p. 102 [English translation: Soviet Electrochemistry, 3 Vols., L. Nanis (editor), Consultants Bureau, New York (1961)].
9. Ya. V. Durdin and A. M. Markevich, Zh. Obshch. Khim., 19, 2132 (1949).
10. E. J. Kelly, J. Electrochem. Soc., 112, 124 (1965).
11. Huo Ngoc Bah and Nguyen-Duk-Hoe, Élektrokhimiya, 4, 990 (1968).
12. R. I. Agladze, N. T. Gofman, and G. I. Darchiani, Élektrokhimiya, 10, 739 (1974).
13. J. O'M. Bockris and S. Srinivasan, J. Electrochem. Soc., 111, 844, 853, 858 (1964).
14. L. I. Krishtalik, Élektrokhimiya, 6, 1456 (1970).
15. L. I. Krishtalik and V. M. Tsionskii, J. Electroanal. Chem., 31, 363 (1971).