BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1744—1747 (1969)

The Surface Rearrangement*[1] of Adsorbed Hydrogen on Platinum Electrodes

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(Received April 24, 1968)

It is an accepted fact that the adsorbed hydrogen waves (ahw) which appear in a current-potential curve obtained by a linear potential sweep experiment with a noble metal electrode are depressed by the competitive adsorption of foreign substances in the solution. This character of the ahw has been utilized to determine the surface coverage of various organic substances[1-4] as well as the carbon monoxide[3,5,6] adsorbed on platinum electrodes. The method employed in these experiment is very useful in determining the relative surface coverage of adsorbent under given conditions. However, because of the competitive adsorption of unavoidable impurities in the solution and also the spontaneous structural change in the ahw itself, it seems inadequate as a basis for discussing in detail either the kinetics of adsorption or the absolute determination of adsorbent.

In the present paper, some basic characteristics of the ahw observed in sulfuric acid solutions containing no additional substance will be described.

Experimental

Super Special Grade sulfuric acid of Wako Pure Chemicals, Ltd., was used as the electrolyte. The tap water was first purified by means of an ion-exchange column and then distilled twice in glass vessels. In order to avoid contamination by foreign anions, a mercury-mercurous sulfate electrode was used as the reference electrode. The potential values in this paper are referred to this electrode. A platinized platinum wire with an apparent area of 0.19 cm^2 was used as the test electrode. Similar results were obtained in comparative experiments with a smooth platinum electrode. Nitrogen gas was bubbled into the solution to remove any dissolved gases. The rate of potential sweep was mainly kept at 0.2 V/sec. Current-potential curves were recorded by means of an XY-recorder, Model XYR-1A, of Toa Electronic Co., Ltd.

Results and Discussion

The curve in Fig. 1 respresents the current-potential curve at the steady state of the potential sweep. The steady-state curve is obtained after repeating the cyclic potential sweep several times, but the curve deforms more or less during the first few cycles of the potential sweep depending on the conditions under which the electrode was stored before use. Once the steady state is attained, the curve form remains unchanged during further repetitions of the sweep. When the sweep is stopped at a given constant potential for a short period of time, the ahw again is deformed during several succeeding cycles of the potential sweep. Some actual observations are shown in Fig. 2. This sort of phenomenon seems to have drawn the attention of several workers,[7-9] and the simultaneous adsorption of contaminants has been held

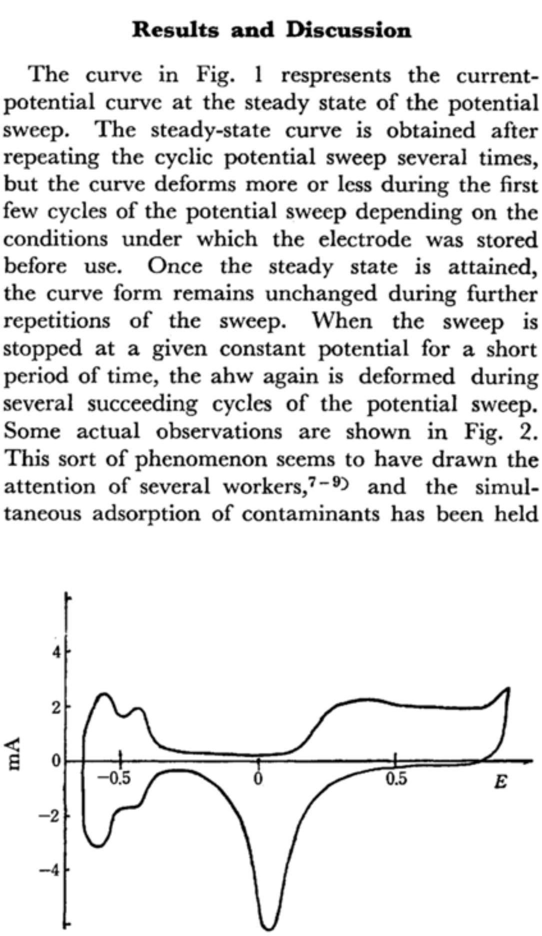

Fig. 1. Steady state current-potential curve in 1 N sulfuric acid solution. Platinized platinum electrode, Sweep rate: 0.1 V/sec, Reference electrode: mercury - mercurous sulfate

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*[1] The authors prefer to use the term "rearrangement" rather than "migration," since it is questionable whether or not the geometric migration actually takes place in the phenomenon reported in this paper.

1) M. W. Breiter *et al.*, *J. Electrochem. Soc.*, **109**, 622, 1099 (1962); **110**, 449 (1963); *J. Electroanal. Chem.*, **14**, 407 (1967).

2) V. S. Bagotzkii *et al.*, *Electrochim. Acta*, **9**, 869 (1964); *Russ. J. Electrochem.*, **1**, 70, 916 (1966).

3) S. B. Brummer *et al.*, *J. Phys. Chem.*, **68**, 1448 (1964); **69**, 562 (1965); **71**, 3494 (1967).

4) S. Gilman, *J. Electrochem. Soc.*, **113**, 1036 (1966).

5) S. Gilman, *J. Phys. Chem.*, **66**, 2657 (1962); **67**, 78 (1963); **71**, 2424 (1967).

6) S. B. Brummer and J. I. Ford, *ibid.*, **69**, 1366 (1965).

7) S. Trasatti, *Electrochim. Metallorum* (Milan), **3**, 1 (1966).

8) W. G. French and T. Kuwana, *J. Phys. Chem.*, **68**, 1279 (1964).

9) S. D. James, *J. Electrochem. Soc.*, **114**, 1113 (1967).

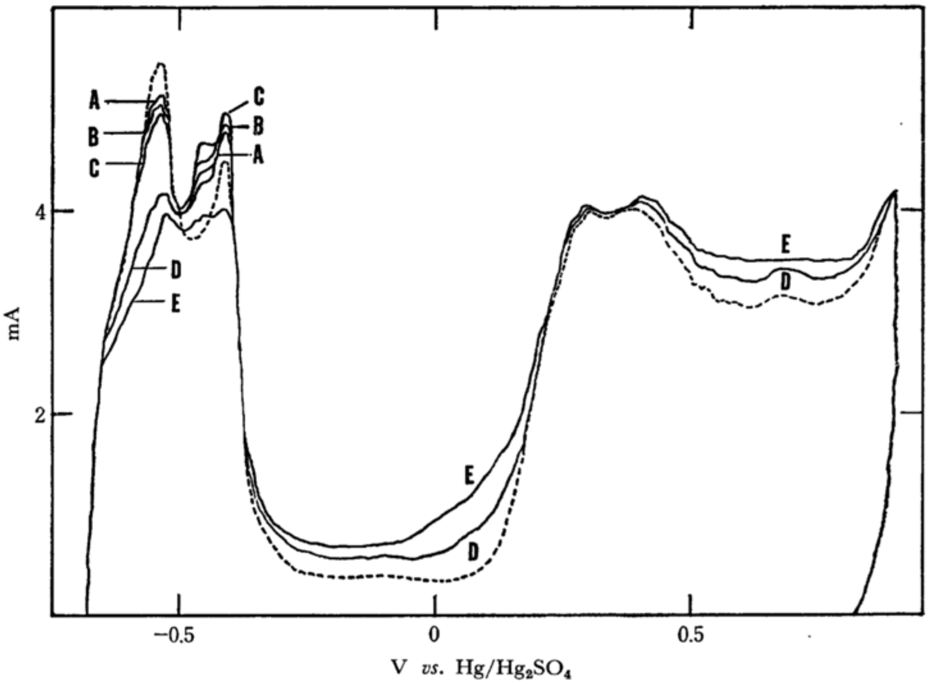

Fig. 2. Effect of the constant potential treatment.
Dashed curve indicates the steady state curve. Curve A was obtained after 5 sec. B, 10 sec; C, 20 sec; D, 25 min; E, 60 min. Curves for 5, 10 and 20 sec merge in the steady state curve at higher potential range. The potential sweep was paused at −0.68 V.

to account for the depression of ahw.[7,9] [*2] A close inspection of Fig. 2 indicates, however, that there is another source of the depression of the ahw. In obtaining the curves in Fig. 2, after the steady state curve(dashed line) had been attained, the potential sweep was stopped at a desired potential (−0.68 V in this case) for various periods of time ("waiting time" will be used hereafter); then the potential sweep was carried out in order to record the full lines of the curves.

It may be seen in Fig. 2 that the left half of the double peak (peak I) diminishes monotonously with the time, while the right half (peak II) first increases and then gradually decreases. After a prolonged treatment at −0.68 V, the ahw becomes a hump-like single peak. Although the depression of the ahw can be attributed to the adsorption of contaminants, the transient increase in peak II requires explanation. Two reasons can be cited for this transient increase: 1) the steady state curve does not represent the saturation coverage of

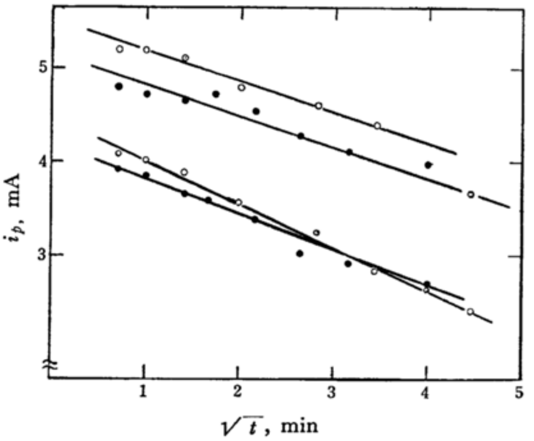

Fig. 3. Decrease in peak current with time.
Full circle: Potential sweep was paused at −0.45 V.
Empty circle: Potential sweep was paused at −0.25 V.
After the constant potential treatment, the electrode was first polarized cathodically and then reversed at −0.68 V to anodic direction. Upper two curves stand for peak I and lower two for peak II.

[*2] French and Kuwana[8] found an essentially similar effect. They attributed the depression of the ahw to the deactivation of platinum atoms at the electrode surface. In the present case, however, the deactivation of the electrode surface does not seem to be the main reason. This was concluded from the fact the decrease in the ahw resulted in an increase in the quantity of electricity at the potential regions of both the double-layer charging and the surface oxide formation. The quantity of electricity recovered at these two potential regions always exceeded that at the ahw (see Fig. 2). This point will be discussed in a later paper.

hydrogen, but rather the adsorption continues during the waiting time, and 2) some of the hydrogen adsorbed at peak I migrates or rearranges*1 to a more stable form at peak II. The former explanation seems unlikely, because the transient increase only appeared in peak II, not at all in peak I.

The transient increase in peak II was not found when the sweep was paused at a potential more negative than the saddle point of the double peak. At these potentials, peak II decreased monotonously with the time. This is illustrated in Fig. 3, where the decrease in the peak current is plotted against the square root of the waiting time. Since the transient increase was found only when the potential sweep was paused at a potential range covered by peak I, it is reasonable to assume that some of the hydrogen adsorbed at peak I migrates to peak II. The following facts support this assumption. The decrease at peak I roughly holds a linear relationship with the square root of the waiting time. The square-root dependence does not, however, hold exactly, and a small deviation arises at a shorter time, as may be seen in Fig. 4. This indicates that the decrease at peak I is caused not only by the diffusion-controlled adsorption of contaminants, but also by something else. It must be noted that the points deviating from linearity in Fig. 4 fit on a straight line when the abscissa is drawn on a logarithmic scale instead of on the basis of the square root (curve A in Fig. 5). Accordingly, the depression of peak I can be approximated by the equation:

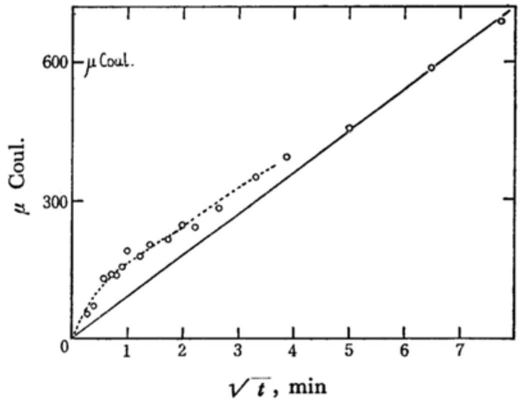

Fig. 4. Decrease of peak I with time.
Potential sweep was paused at -0.68 V.

$$\Delta q_{\mathrm{I}} = -kt^{1/2} + k' \log t \tag{1}$$

where Δq_{I} represents the difference in the quantities of electricity between the steady state curve and the curve obtained after the waiting time, t. The negative signs in the right-hand side terms were given to express the decrease at the ahw. k should be the sum of the diffusion coefficients (not the diffusion constants) of the contaminants, and k', the rate constant of the rearrangement of the adsorbed hydrogen. The behavior of peak II in Fig. 2 suggests that there might be two counteracting processes. The curve B in Fig. 5 shows this in more detail. Of course, it is reasonable to assume the counteracting processes to be the contaminant adsorption and the surface rearrangement of the adsorbed hydrogen. Thus, the rate of change at peak II can be expressed as:

$$\Delta q_{\mathrm{II}} = -kt^{1/2} + k' \log t \tag{2}$$

By combining Eqs. (1) and (2), the effect of the contaminant adsorption can be cancelled:

$$q_R = \Delta q_{\mathrm{II}} - \Delta q_{\mathrm{I}} = 2k' \log t \qquad (3)^{*3}$$

where one half of q_{R} represents the amount of hydrogen rearranged from peak I to peak II.

Curve C in Fig. 5 shows the difference between Δq_{II} and Δq_{I}. In accord with the expectation from Eq. (3), the curve shows a linear relationship with log t when t does not exceed twenty to thirty minutes. At a longer waiting time, the curve become flat (although this part is not seen in Fig. 5), thus indicating the equlibrium of the rearrangement. The total amount of hydrogen which takes part in the rearrangement was found to be less than 10% of the adsorbed hydrogen at saturation.

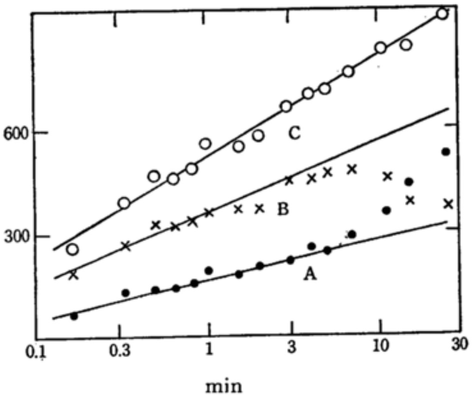

Fig. 5. Curve A: Decrease of peak I, B: Incerase of peak II C: Corrected change at peak II.

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*3 In the above discussion, k' was taken to be common to both Δq_{I} and Δq_{II}. The treatment is, therefore, equivalent to assuming that no hydrogen adsorbs on vacant sites produced after the rearrangement. Actually, this is not true, since it was found that the increase in the charge at peak II (Δq_{II}) was greater than the decrease at peak I (Δq_{I}) unless the waiting time exceeded thirty seconds or so. Accordingly, Eq. (1) will require an additional term to express the adsorption on vacant sites produced after the rearrangement. Because cf the present lack of experimental accuracy, however, it seems meaningless to attempt to discuss the mechanism in such detail.

In order to find the activation energy of the process, experiments were carried out at three different temperatures, 5, 25, and 40°C. The results indicated that the activation energy, if it existed, was less than 1 kcal/mol.