Discharge of Hydrogen Ions at Metal Cathodes in Alkaline Solutions

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A survey is given for the measured pH effects in alkaline solutions on hydrogen overpotential. The results are not in accord with the theoretical value for H^+ ion discharge, or with that for the discharge of water molecules. This problem arises from neglecting the role of the stoichiometric number of the reaction in the rate equation.

It is suggested that H^+ ions are discharged, and the adsorbed hydrogen atoms undergo rapid catalytic combination. In this case the stoichiometric number is 2, and the reaction order with respect to H^+ ion is 1/2. This mechanism requires that the overpotential is independent of the alkali concentration. The mechanism accounts satisfactorily for the slight changes in overpotential with the alkali concentration.

Evolution of hydrogen at metal cathodes from acid solutions takes place through the discharge of H^+ ions. In alkaline solutions, however, hydrogen might originate from the discharge of H^+ ions, or from the discharge of water molecules. Distinction between these two entities could be made with the help of the effect of pH on the overpotential η. For the discharge of H^+ ions (in the absence of specific adsorption and when the potential is far from that of the electrocapillary maximum), the dependence of η at the constant current density i on pH is given by the equation

$$\left(\frac{\partial \eta}{\partial \text{pH}}\right)_i = -\frac{2\,(2.303\,RT)}{F} \tag{1}$$

This indicates that η decreases (becomes more negative) by 120 mV per unit increase of pH at 30 °C. For the discharge of water molecules, assuming the activity of water molecules in the double layer to be equal to their activity in the bulk, one gets

$$\left(\frac{\partial \eta}{\partial \text{pH}}\right)_i = \frac{2\,(2.303\,RT)}{F} \tag{2}$$

indicating that η increases (becomes less negative) by 120 mV per unit increase of pH.

For many metal cathodes, positive pH effects were obtained, but the observed results did not agree with the theoretically deduced values. Thus, for a nickel wire Bockris and Potter [1] observed a pH effect ranging from 10 to 25 mV per unit increase of pH (see also Ref. [2]). For copper cathodes, in moderate alkali concentrations, Bockris and Pentland [3] obtained a pH effect of 29 mV. In the case of electrodeposited nickel, Ammar and Awad [4] reported

a value of 26 mV, whereas for silver [5] they observed that the pH effect lies between 25 and 30 mV. It is obvious from this survey that the experimental pH effects are too small to indicate exclusively the discharge of water molecules.

It is worth mentioning that in case of mercury the pH effect in dilute alkaline solutions amounts to 105 mV [6]. However, it had been shown by Bockris and Watson [7] that the discharged species at the mercury cathode is the Na^+ ion, and not the water molecule. Hydrogen is then formed through the chemical interaction of the amalgam with water.

In an attempt to correlate the experimental results for the pH effect in alkaline solutions with the theory, Bockris and Potter [1] have suggested the possibility of an increase in the activity of water molecules in the double layer as compared to that in the bulk of solution. This is brought about by the orientation of water molecules under the high field strength near the electrode. Taking this suggestion into consideration, Ammar and Awad [5] obtained a theoretical pH effect for silver cathode, which is again quite different from the observed values.

It is evident from the foregoing discussion that there is no sharp decision about the species discharged at the cathode. However, Parsons and Bockris [8] have proposed that the discharge of water molecules is more probable than the discharge of hydrogen ions. This is because the concentration of the former species is much larger than the concentration of the latter one. But the concentration term is not all, there remains the activation energy of the reaction. It is expected that the heat of activation for the neutralization of the proton in the water molecule is remarkably larger than that for the neutralization of the proton in the hydroxonium ion. The observed values of ΔH^* in acid solutions are, however, comparable with

those observed in alkaline solutions; both amounting to ≈ 41.8 kJ mol^{-1}. This behaviour favours, on the other hand, the discharge of hydrogen ions.

DISCUSSION

The puzzling problem in the cathodic evolution of hydrogen from alkaline solutions is that the pH effect differs markedly from the values expected for both H$^+$ ions and water molecules. It is observed, however, that the number of occurrences of the rate-determining step per one act of the overall reaction (*i.e.* the stoichiometric number) was not taken into consideration in the rate expression. This is not correct according to the theory of multi-step electrochemical reactions [9].

Let us consider the discharge of H$^+$ ions. If the first step

$$H^+ + e \longrightarrow H \qquad (A)$$

is the slowest one, the reaction rate as a function of the concentration depends upon whether the hydrogen atoms are desorbed chemically or electrochemically.

In the case of chemical desorption

$$H + H \longrightarrow H_2 \qquad (B)$$

the slow step (*A*) proceeds twice for one occurrence of the overall reaction (*B*). Here, the reaction rate depends on the square root of the hydrogen ion concentration. Hence, the expression for the cathodic current is

$$i = k\left[H^+\right]_{dl}^{\frac{1}{2}} \exp\left(\frac{-\alpha\Delta\phi F}{RT}\right) \qquad (3)$$

where $[H^+]_{dl}$ is the concentration of the hydrogen ion in the double layer, $\Delta\phi$ is the potential difference between the cathode and the Helmholtz layer, and α is the transfer coefficient.

In the case of the electrochemical desorption

$$H + H^+ + e \rightarrow H_2 \qquad (C)$$
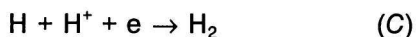
the slow step (*A*) proceeds once per one occurrence of the overall reaction. Hence, the rate of the overall reaction is proportional to the hydrogen ion concentration and the cathodic current is given by

$$i = k\left[H^+\right]_{dl} \exp\left(\frac{-\alpha\Delta\phi F}{RT}\right) \qquad (4)$$

Substituting in eqn (*3*) $[H^+]_{dl}$ by $[H^+] \exp(-\zeta F/RT)$, where $[H^+]$ is the concentration in the bulk of solution and ζ is the zeta potential, and $\Delta\phi$ by $(\Delta\phi_r + \eta - \zeta)$, where $\Delta\phi_r$ is the reversible potential, and taking α as 0.5, one gets

$$i = k\left[H^+\right]^{\frac{1}{2}} \exp\left(\frac{-\zeta F}{2RT}\right) \exp\left(\frac{-\Delta\phi_r F}{2RT}\right) \cdot$$
$$\cdot \exp\left(\frac{-\eta F}{2RT}\right) \exp\left(\frac{\zeta F}{2RT}\right) \qquad (5)$$

It follows that

$$\frac{2RT}{F} \ln i = \text{const} + \frac{RT}{F} \ln\left[H^+\right] - \Delta\phi_r - \eta \qquad (6)$$

The potential of the reversible electrode is equal to $RT/F \ln [H^+]$, and hence, at a given current density

$$\eta = \text{const} \qquad (7)$$

Eqn (*7*) requires that the overpotential is independent of pH. Application of similar mathematical treatment to eqn (*4*) yields relation (*1*).

If the cathode reaction involves water molecules, then introduction of $[H_2O]^{1/2}$ instead of $[H_2O]$ does not make any difference and the pH effect is still given by eqn (*2*), whether the hydrogen atoms are desorbed chemically or electrochemically.

The fact that, except in case of Hg, the overpotential changes but slightly with the alkali concentration, indicates that H$^+$ ions are discharged and the atoms are desorbed chemically.

REFERENCES

1. Bockris, J., O'M. and Potter, E. C., *J. Chem. Phys. 20*, 614 (1952).
2. Frumkin, A. N., *Zh. Fiz. Khim. 24*, 244 (1950).
3. Bockris, J., O'M. and Pentland, N., *Trans. Faraday Soc. 48*, 833 (1952).
4. Ammar, I. A. and Awad, S. A., *J. Electrochem. Soc. 104*, 686 (1957).
5. Ammar, I. A. and Awad, S. A., *J. Phys. Chem. 60*, 1290 (1956).
6. Kaptsan, O. L. and Jofa, S. A., *Zh. Fiz. Khim. 26*, 193, 201 (1952).
7. Bockris, J., O'M. and Watson, R. G. H., *J. Chim. Phys. 49*, C70 (1952).
8. Parsons, R. and Bockris, J., O'M., *Trans. Faraday Soc. 47*, 914 (1951).
9. Bockris, J., O'M. and Reddy, A. K. N., *Modern Electrochemistry*, Vol. 2, p. 1006. Plenum Press, New York, 1977.