SOME REFLECTIONS ON THE STUDIES OF CATHODIC EVOLUTION OF HYDROGEN FROM ALKALINE SOLUTIONS

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The effect of pH on cathodic evolution of hydrogen at different metals in alkaline solutions is surveyed and discussed. It is shown that the discharge of H^+ ions is more probable than the discharge of water molecules. The anomalous pH effect and reaction order are ascribed to variations of negative and positive metallic species at the electrode surface. Disproportionation of metallic atoms might contribute to the formation of these species.

pH Effect and Reaction Order

Evolution of hydrogen at metal cathoes 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, and under conditions when the change of zeta potential, ξ , with concentration is neglected, the dependence of η, at constant density, on pH is given by [1].

$$\left[\frac{\partial \eta}{\partial pH}\right]_i = -\frac{2.303RT}{F} \qquad \ldots (1)$$

This indicates that η decreases (becomes more negative) by 60 mV per unit increase of pH at 30°C. For the discharge of water molecules, assuming the activity of water in the double layer to be equal to its activity in the bulk, one gets:

$$\left[\frac{\partial \eta}{\partial pH}\right]_i = \frac{2.303RT}{F}, \qquad \ldots (2)$$

indicating that η increases (becomes less negative) by 60 mV per unit increase of pH. Hence the sign of the pH effect was considered a good criterion for distinguishing between the species discharged.

For many metal cathodes, positive pH effects were obtained, but the observed values did not agree with the theoretically deduced value as given by equation (2). Thus, for nickel wire Bockris and Potter [1] observed a pH effect ranging from 10 to 25 mV per unit increase of pH, whereas a value of 40 mV was determined by Lukovzew and Lewina [2]. For electrodeposited nickel a pH effect of 26 mV was reported by Ammar and Awad [3]. The same authors observed that the pH effect for silver [4] lies between 25 and 30 mV. Studies on aluminium carried out by Kamel and co-workers [5] gave a value of 28 mV. It is obvious that the experimental values did not coincide with the value required for H^+ ions, nor with that for water molecule.

It is perhaps more useful to express the results in terms of reaction orders. Neglecting again the change in ξ potential, the reaction order can be evaluated by determining the change in the logarithm of current density with respect to the change in pH at a constant potential, viz, $\left(\frac{\partial \log i}{\partial pH}\right)_E$. Thus, for rate-determining discharge reaction involving H^+ ion:

$$H^+ + e \longrightarrow H, \qquad \ldots (3)$$

the reaction order, with respect to pH, should be -1. For a rate determing discharge reaction involving water molecule:

$$H_2O + e \longrightarrow H + OH^-, \qquad \ldots (4)$$

the order is zero. The experimental data for electrodeposited Ni[3], Ag[4] and Al[5] denote a reaction order of about -0.3; a value which is again different from the values expected for H^+ ion and water molecule discharge. From the observed reaction order one concludes that if the reacting entities were the H^+ions then, increase of the alkali concentration exerts some sort of acceleration on the cathode reaction, since the order is increased from -1 to -0.3. On the other hand, if the water molecules are involved, the reaction is subjected to some decelerating action, since the order decreases from 0 to -0.3. One may think about this deceleration as being due to smaller

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activity of water molecules in the double layer in comparison to the bulk activity. Unfortunately, Bockris and Poter [1] expected higher activity of water molecules in the double layer, owing to the high field strength operating in this region, leading to the orientation of water dipoles.

It is evident from the foregoing discussion that there is no sharp decision about the species discharged at the cathode. However, on the basis of some kinetic considerations, Parsons and Bockris [6] have proposed that in alkaline solutions the discharge of water molecules is more proable than the discharge of H^+ ions. This is because the supply of H^+ ions from the bulk of solution to the electrode would be slow.

Effect of nitric ion on the kinetics of hydrogen evolution

Recently, the behaviour of aluminium cathodes in NaOH solutions containing 10^{-4} - 1 M $NaNO_2$ was investigated [7], with the hope of studying the mechanism of reduction of the nitrite ion. However, within the concentration range studied, there occurred no reduction of NO_2^- ions, and the cathodic reaction was nothing but hydrogen evolution with Tafel slope of 0.04 V. Since the Tafel slope in pure NaOH solutions is about 0.12 V [3,4,5,8], (which is characteristic for slow discharge mechansim [9], it was concluded that the nitrite ion modifies the kinetics of hydrogen evolution, perhaps through the formation of an intermediate reduction product. Up to this point there is nothing peculiar. But we were greatly surprised to obtain a reaction order of -2.3; a value which excludes the participation of water moelcules in the cathode reaction, and indicates beyond doubt that H^+ ions are involved instead. Hence, a mechanism was formulated, that led to the expression [7].

$$i = k[NO_2^-][H^+]^2 \exp(-\frac{3EF}{2RT}) \quad \ldots (5)$$

This expression satisfied the requirement of Tafel slope = 0.04 V and reaction order (with respect to pH) = -2. It was also surprising that the Tafel relations are extended linearly up to 10^{-2} A/cm^2, without any indication whatsoever to slow supply of H^+ions. Consequently, there remained no reason to consider the discharge of water molecules, in case of pure NaOH solutions, as more probable. Therefore, we belive that, in analogy to solutions containing nitrite, evolution of hydrogen from pure alkaline solutions takes place through the discharge of H^+ ions.

Effect of the cathode surface on reaction order

Having arrived at the conclusion that H^+ ions are discharged, we have to account for the following phenomena:

First, the acceleration exerted on the cathode reaction, leading to the increase of reaction order from -1 to -0.3 as mentioned above.

Secondly, the disappearence of this acceleration in presence of nitrite ions, such that the experimental reaction order agrees fairly with the theoretical value (cf. equation 5).

The second phenomenon points out to the possibility that H^+ ions are discharged at areas which are not suitable for the reduction of nitrite ions. Therefore, and for a reason to be clarified soon below, it is suggested that, beside the neutral atoms, the metal surface contains positive and negative ions, formed according to

$$M \rightleftharpoons M^+ + e \quad \ldots (6)$$

$$M + e \rightleftharpoons M^- \quad \ldots (7)$$

An equilibrium is established between these ions and the metal atoms. The number of the different species at the metal surface depends on potential; thus, increase of potential favours the increase of the positive ions, while decrease of potneital favours the formation of the negative ions. M^+ and M^- represent centers for different cathodic reactions. Thus, a reducible negative anion, like NO_2^-, is reduced at a positve center, which acts as an electron bridge between the interior of the metal and the reducible species. On the other hand, H^+ ions are reduced at negative centers. One would expect that the rate of an electrochemical reaction depends, not only on the activities of reactants in solution but also on the number of the appropriate centers on the electrode surface. It follows that equations describing the kinetics of electrochemical reactions are expected to apply strictly only when the appropriate centers on the electrode surface do not undergo considerable changes. In case of cathodic hydrogen evolution, increase of the alkali concentration shifts the reversible potential to more negative values; and it seems that this causes considerable increase of negative centers. It follows that the reaction is subjected to marked acceleration, and the electrochemist faces the difficulty of inapplicability of the reaction rate expression.

In presence of nitrite ions the reaction is initiated on the positive centers, M^+. Since the number of these centers decreases with the alkali concentration, one expects deceleration (and not acceleration) of the reaction. We can have an idea about the extent of deceleration from the following arugment. From equations (6) and (7), we can obtain.

$$\frac{[M^+][M^-]}{[M]^2} = K \qquad \ldots (8)$$

If we neglect the change in the number of atoms, equation (8) shows that the product of positive and negative centers is kept constant, in exactly the same manner as the product of H^+ and OH^- ions in aqueous solutions. When $[H^+] \approx [OH^-]$, i.e., in neutral solutions, an increase in the amount of one species leads to a nearly equal decrease in the amount of the other species. But when one ion is found in excess, eg., the hydroxyl ion in alkaline solutions then large increase in $[OH^-]$ brings about only slight decrease of $[H^+]$. In an analogous manner, if in alkaline solutions the cathode surface contains excess of M^-, then large increase in the number of this species leads to slight decrease in the number of M^+. Hence, the reaction rate is slightly decelerated. This is actually the case, as obvious from the experimental reaction order (-2.3), which is slightly smaller than the expected value (-2).

In conclusion, it might be useful to have a deeper look at equation (8). This equation corresponds to a chemical process of the form.

$$2M \rightleftharpoons M^+ + M^- \qquad \ldots (9)$$

It is, thus, probable that, in addition to the independent formation of positive and negative species according to equations (6) and (7), these species might be formed, at least in part, through the disproportionation of the surface metal atoms.

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LIST OF SOME OF THE SYMBOLS USED IN THIS JOURNAL

A	-	ampere
a	-	activity
C	-	coulomb
°C	-	degree celsius
c	-	concentration in general
D	-	diffusion coefficient
d.c.	-	direct current
E	-	potential
E°	-	standard electrode potential
$E_{1/2}$	-	half wave potential (polarographic)
F	-	Faraday constant
ΔG	-	Gibbs free energy change
ΔH	-	enthalpy change
I	-	current, ionic strength
J	-	Joule
J	-	current density
K	-	Kelvin
k	-	equilibrium const
k	-	rate const.
l	-	litre
ln	-	natural logarithm
log	-	decimal logarithm
M	-	molar concentration (no of moles of solute/litre of solution)
m	-	meter
m	-	molal concentration (no of moles of solute per 1000 g of solvent)
N	-	normality
s	-	second
T	-	absolute temperature
t	-	temperature, celcius
t_x	-	cation transport no
u	-	ionic mobility
V	-	volt Ω Ohm
Σ	-	relative permittivity
ξ	-	electro kinetic potential (Zeta potential
η	-	over voltage
$\varkappa$	-	(kappa specific conductance)
$\Lambda_\pm$	-	equivalent conductivity of electrolyte
$\lambda_\pm$	-	ionic equivalent conductivity
$\tilde{\upsilon}$	-	(tou time)