The Reduction of Hydrogen on Pure Nickel Electrode in Sulphuric Acid

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The reaction of hydrogen evolution (HER) in 1.2 and 3 M H_2SO_4 at 303°, 313° and 323°K has been studied. The results and analysis showed that the cathodic current density, the cathodic Tafel slope and the exchange current density are dependent on temperature and acid concentration. The mechanism of the hydrogen evolution is: rate-determining discharge followed by electrodic desorption.

The hydrogen evolution reaction (HER) is of fundamental importance in electrochemistry. It is the basis of the electrolytic production of hydrogen and this is the rate determining step (rds) in the acid corrosion of many active metals. Its mechanism and kinetics are receiving increasing attention now since it is recognized as a central step in the mechanism of hydrogen embrittlement of iron base alloys [1].

The exchange current density of the 'HER' depends critically on the nature of the electrode material; it increases by a factor of 10^{10} from Pb to Pd [2]. It also depends on the composition of the electrolyte. The presence of trace impurities in the electrode material influences the kinetics of this reaction. The objective of the this work was to study the reaction of hydrogen evolution on nickel in 1, 2 and 3 M H_2SO_4 and determine the exchange current density as well as the cathodic Tafel slope at various temperatures.

EXPERIMENTAL

The electrode was in the form of a sheet of pure nickel (99.9+%). It was polished successively down to 0 grade. A saturated calomel reference electrode was used. The measurements were taken potentiostatically using potentiostat type (Model 553, from AMEL Italy). Further details of the cell and the experimental procedures are available elsewhere [3].

RESULTS AND DISCUSSION

The Cathodic Region

The parameters involved in the study were temperature and acid concentration. The cathodic curves shown in Fig. 1 were obtained by polarizing the specimen starting from negative towards positive potentials, thereby decreasing the cathodic overpotential. In general, the curves show a curvilinear relationship between electrode potential and the logarithm of the current density.

The effect of temperature and concentration on the cathodic current density at a given cathodic potential are shown in Table 1. Concentration polarization due to hydrogen evolution in this case was avoided by choosing a potential faraway from the corrosion potential (-500 mV). The corresponding current density values were read from Fig.

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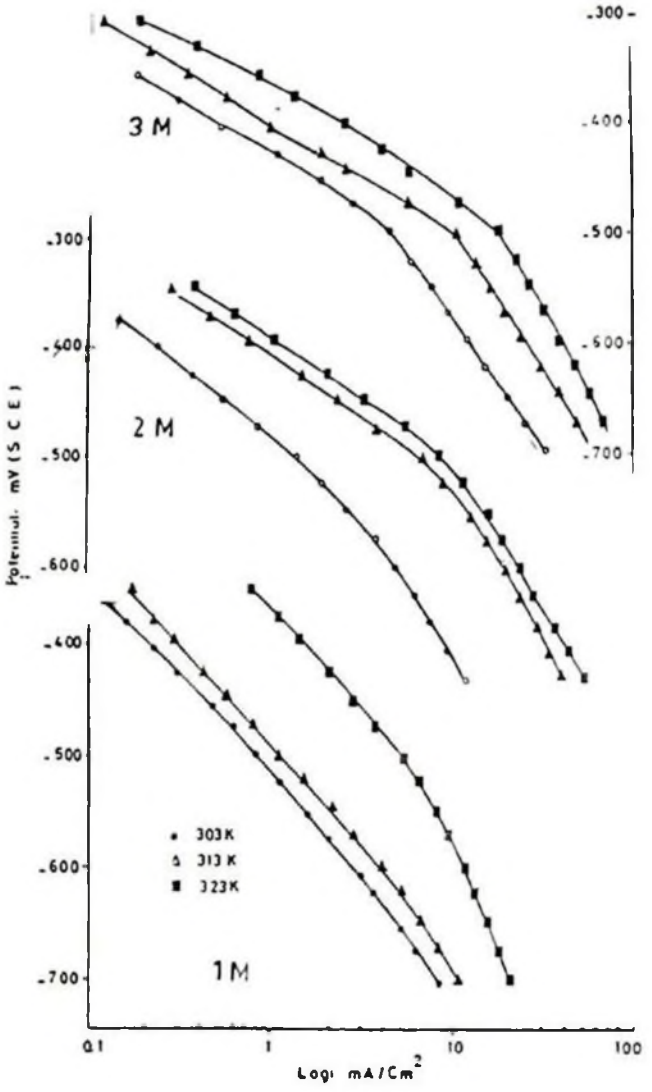


Fig.1 Cathodic Polarization Curves in H_2SO_4 Solutions at different termpretures

Table 1

The Current Density (I) at different Temperatures and diffrent acid concentration

Potential - 500 mV

H_2SO_4	I (mA/cm²) at		
M	303° K	313° K	323° K
1	0.85	1.1	5.6
2	1.45	7.0	8.2
3	4.7	11.3	19.0

The data in Table 1 has been analysed by the method of variance described by Moroney [4] and applying Null hypothesis. The results show that the cathodic current density is dependent both on temperature and acid concentration. The discharge of the proton upon the nickel surface can be considered as the rate determining step in the hydrogen evolution reaction [5]. The rate determining step is itself controlled by the reduction of proton upon the surface which is charge transfer controlled and normally affected by temperature.

$$H_3O^+ + e \longrightarrow H_{ads} + H_2O \quad — (1)$$

The reaction rate can obviously be increased by increasing the H_3O^+ supply rate, viz acid concentration. So cathodic current density is dependent both on temperature and acid concentration.

Increasing the temperature at constant acid concentration stimulates the cathodic current density over the cathodic potential range studied. This can be explained by the following equation:

$$\eta_c = -b_c \log i/i_o \quad ..... \quad (2)$$

b_c values were obtained from Fig 1. An increase in b_c thus yields a decrease in the quotient $(-\eta_c/b_c)$ and hence, the current density i increases.

Table 2

The cathodic Tafel Slope values (b_c)at different Temperatures and diffrent acid concentration

H_2SO_4	(b_c) mV/decade at		
M	303°K	313°K	323°K
1	114	122	128
2	118	123	135
3	107	114	121

The exchange current density, i_o, for hydrogen reaction (at the reversible potential) on nickel electrode is also influenced by temperature [6]. The reversible thermodynamic potential of hydrogen electrode, E_{H/H^+}, at various acid concentrations was calculated using equation :

$$E_{H/H^+} = - (RT/zF) \ln (1/a_{H^+})$$

where a_{H^+} = the activity of hydrogen ions.

The required data of the activity coefficient values at various acid concentrations were obtained from literature [11]. The values are 0.808 at 1 M, 1.01 at 2 M and 1.32 at 3 M.

The exchange current density values were calculated using equation 2 and the results are shown in Table 3.

Table 3.

The exchange current density of 'HER' (i_o)
Electrode Nickel; Sulphuric Acid medium; Temperature Varying

H_2SO_4 M	——i_o Amp/cm² x 10^6 at —— 303°K	313°K	323°K
1	1.4	2.3	13
2	4.3	21.6	36
3	10.2	29.6	58.4

The above Table showes that the exchange current density increases with the increase in temperature and acid concentration, therefore, stimulates the rate of cathodic reaction at a given potential.

Mechanism of the Hydrogen Evolution

The transfer coefficient (α) and the stoichiometric number (γ) values have been calculated at various temperatures and acid concentrations from Tafel slope values [12] and the results are shown in Table 4.

Table 4.

The Transfer Coefficient, α and the Stoichiometric Number γ at Different Temperatures

H_2SO_4 M	303°		313°		323°	
	α	γ	α	γ	α	γ
1	0.52	0.94	0.51	0.98	0.48	1.05
2	0.51	0.98	0.51	0.98	0.50	1.00
3	0.56	0.89	0.54	0.93	0.59	0.97

Table 4 shows almost constant value for the transfer coefficient and the stoichiometric number within the studied range of tempeatures (303-323°K) and the acid concentration values (1-3 M). The stoichiometric number is taken as =1 (since it cannot be a fraction). The transfer coefficient can be considered equal to 0.5. The following table [5] gives the defferent mechanisms and the corresponding values of transfer coefficient and the stoichometric number.

Comparing the values obtained from the experimental result with the values in Table 5, the mechanism of hydrogen evolution is taken to be rate determining discharge followed by electrodic desorption, as follows:

Rate determining step

$$H_3O^+ + e \longrightarrow H_{ads} + H_2O \quad \ldots\ldots (3)$$

followed by

$$H_{ads} + e + H_3O^+ \longrightarrow H_2 + H_2O \quad \ldots\ldots (4)$$

where e is an electron transfered from the nickel surface.

Table 5

The transfer coefficient α and the stoichometric number γ values for some Hydrogen- Evolution Mechanims

Mechanism	Tr. coeff for $\beta = 0.5$	γ
1. Rate determining discharge followed by chemical adsorption.	0.5	2
2. Discharge followed rate-determing chemical desorption	2	1
3. Rate determining Discharge followed by electrodic desorption	0.5	1
4. Discharge followed by rate-determining electrodic desorption	1.5	1

The above mechanism is in agreement with that reported by Bockris et al [8] in 0.1 N sulphuric acid solution in the temperature range (291-353°K). Meyrevsky, as quoted by Daft et al [9], suggested a similar mechanism of hydrogen evolution in acid media.

CONCLUSIONS

1. The hydrogen evolution showed temperature and acid concentration dependency. As the temperature and/ or acid concentration increases, the values of hydrogen reduction rate, the Tafel slope and the exchange current density increase.

2. The mechanism of hydrogen evolution in the studied system is: discharge-rate determining followed by electrodic desorption.

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