

The Catalytic Properties of Black Nickel Hydrogen Electrodes

Part I. Galvanostatic Studies of the Proton Discharge Reaction on Black Nickel Electrodes

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Pure nickel sheets have been plated with black nickel deposits, and electrodes of various shades are produced by varying the plating current or the plating time. These black nickel electrodes are used as hydrogen electrodes in 1 N KOH, and the behaviour of the electrodes is experimentally examined at small current densities. A galvanostatic method is used in order to determine the exchange current density, i_0 , for the discharge reaction, the differential capacity, C , and the number of adsorbed hydrogen atoms on the electrode surface. The relation C/i_0 is measured to be the same for all electrodes, indicating that the electrodes differed only in their effective surface areas, and that they possessed the same kind of catalytic active sites with respect to the discharge reaction.

The basic theoretical equations are published earlier,¹ but more complete and general solutions are given in the present paper.

Three main reactions are considered for the hydrogen evolution reaction on nickel electrodes in alkaline solutions. The first step is the discharge of a proton from a water molecule to yield adsorbed atomic hydrogen on the surface (the discharge reaction). This adsorption step may be succeeded by two alternative desorption steps. The adsorbed hydrogen atom can be combined with a hydrogen atom from a further proton discharge reaction (the electrochemical reaction or the secondary discharge reaction) or with a hydrogen atom adsorbed in the neighbourhood, to yield a hydrogen molecule. The general problem is to find the reaction path and to identify the rate-determining step. Detailed experimental and theoretical studies of the mechanism, including the reverse reactions, on nickel and electrodeposited nickel electrodes have been published in the literature.¹⁻⁷

The problem of greatest practical interest is, however, to find how the preparation or pretreatment of the electrodes affects the overvoltage. It is evident from the strong dependence of the overvoltage on the preparation that the rate determining step occurs at the electrode surface, and that the significant properties which must be considered are surface properties. Irrespective of a

detailed knowledge of the surface structure, it can be postulated that the catalytic activity of the electrode is associated with the existence of active sites on the surface, and that each single point possesses an amount of catalytic power with respect to the reaction under examination. The factors which determine the resulting experimental behaviour of the electrode are then the number of active sites per unit area, and the amount of catalytic power associated with them.

In earlier work there has been a tendency to attach a particular mechanism to each individual metal. The electrodes are then only characterized by the catalytic properties associated with the basic metal and their individual roughness factors. It is well known, however, that electrodes which are prepared to give very active surfaces have properties different from "smooth" electrodes of the same basic metal.

A detailed study of the dependence of the cathodic hydrogen evolution reaction on the preparation of the electrode will therefore be of great interest. In this work, the properties of electrodes within a group of black nickel electrodes are studied.

EXPERIMENTAL

The experiments were carried out on black nickel electrodes operating as hydrogen electrodes in carbonate-free 1 N KOH solution. The electrolytic cell is described elsewhere.¹

Preparation of black nickel electrodes. Spectrographically pure nickel sheets were plated with black nickel deposits from a solution containing 33 g/litre of nickel ammonium double sulphate and 14 g/litre of potassium sodium tartrate at a temperature of 20°C.⁸ The plating was carried out at constant current density. Electrodes with deposits of various shades were produced by varying the plating current or the plating time from electrode to electrode. The electrodes were classified in two main groups. In group I, the electrodes were plated at different current densities, ranging from 40 to 220 mA/cm², with 20 mA/cm² increments. The plating time was 50 sec. In group II, the electrodes were plated at the same current density, 100 mA/cm², but the plating time was different from electrode to electrode, ranging from 10 to 120 sec, with 10 sec increments.

The prepared electrodes were rinsed, immersed in 1 N KOH and finally polarized by an anodic current.⁹ Before the experimental runs, the electrodes were reactivated by a cathodic current in the electrolytic cell.

Procedure. The electrolytic solutions were prepared from Merck's reagents (extra pure quality), and distilled water, specific conductivity 10⁻⁶ mhoscm⁻¹. Carbonate-free KOH solution was prepared by a method described by Powell and Hiller.¹⁰ Purified hydrogen, deoxygenated by passing through a palladized asbestos furnace, was obtained commercially in gas cylinders.

The KOH solution was transferred under hydrogen atmosphere to the electrolytic cell. Pre-electrolysis was carried out in the cell using a black nickel cathode and a platinum anode, and continued for about 20 h at a current of 10 mA. The cathode used for pre-electrolysis was then replaced by the black nickel test electrode.

The potential of the electrode was measured against a black platinum hydrogen electrode in the same solution. Starting with the open circuit voltage, the growth of the voltage after switching on a constant current was recorded by a medium speed recorder and a high speed oscilloscope. The current was then interrupted and the electrode potential allowed to reach its steady state rest potential before the next run. Measurements were made in the current range of 1 to 100 μ A/cm². The cell was maintained at a temperature of 20°C throughout the experiments.

BASIC THEORY

The hydrogen overvoltage and the discharge reaction. The activation overvoltage is primarily associated with the two discharge reactions (commonly referred to as the discharge and the electrochemical reaction). If only three variables are considered, the macroscopic law for the reaction current at constant temperature may be written¹

$$i_r = i_{01} \left\{ \frac{1-x}{1-x_0} \exp[-\alpha(zF/RT)\eta] - \frac{x}{x_0} \exp[(1-\alpha)(zF/RT)\eta] \right\} \\ + i_{02} \left\{ \frac{x}{x_0} \exp[-\beta(zF/RT)\eta] - \frac{1-x}{1-x_0} \exp[(1-\beta)(zF/RT)\eta] \right\} \quad (1)$$

where i_r is the net reaction current density for the two discharge reactions, η the overvoltage, and x the fraction of the available surface covered with adsorbed hydrogen atoms. $x = x_0$ and $\eta = 0$ are the steady state values when $i_r = 0$. i_{01} and i_{02} are the exchange current densities for the discharge and the electrochemical reaction respectively. The constants α , β , z , F , R , and T have their usual meaning. In the steady state, the rate of adsorption equals the rate of desorption

$$i_{01} \left\{ \frac{1-x}{1-x_0} \exp[-\alpha(zF/RT)\eta] - \frac{x}{x_0} \exp[(1-\alpha)(zF/RT)\eta] \right\} = \\ = i_{02} \left\{ \frac{x}{x_0} \exp[-\beta(zF/RT)\eta] - \frac{1-x}{1-x_0} \exp[(1-\beta)(zF/RT)\eta] \right\} \quad (2)$$

The time dependence of the overvoltage. If the external current, i , is a function of time

$$i(t) = i_{01} \left\{ \frac{1-x}{1-x_0} \exp[-\alpha(zF/RT)\eta] - \frac{x}{x_0} \exp[(1-\alpha)(zF/RT)\eta] \right\} \\ + i_{02} \left\{ \frac{x}{x_0} \exp[-\beta(zF/RT)\eta] - \frac{1-x}{1-x_0} \exp[(1-\beta)(zF/RT)\eta] \right\} - C(d\eta/dt) \quad (3)$$

where C is the differential capacity.

The rate of change of the degree of coverage, x , is given by the difference between the rate of adsorption and the rate of desorption

$$C_H(dx/dt) = i_{01} \left\{ \frac{1-x}{1-x_0} \exp[-\alpha(zF/RT)\eta] - \frac{x}{x_0} \exp[(1-\alpha)(zF/RT)\eta] \right\} \\ - i_{02} \left\{ \frac{x}{x_0} \exp[-\beta(zF/RT)\eta] - \frac{1-x}{1-x_0} \exp[(1-\beta)(zF/RT)\eta] \right\} \quad (4)$$

where C_H is the adsorption capacity = $n_a \times 1.6 \times 10^{-19}$ coulomb. n_a is the number of free sites available for adsorption of atomic hydrogen on the electrode surface.

Eqns. (3) and (4) describe the time dependence of the overvoltage, η , at any given external current, $i(t)$. If $i(t)$ is a step function, and we start with the open circuit potential, eqns. (3) and (4) describe the time dependence of

the overvoltage at constant current i , with the initial conditions $\eta = 0$ and $x = x_0$.

Eqns. (3) and (4) can be simplified if $|\eta| \ll (RT/zF)$

$$i = -(i_{01} + i_{02})(zF/RT)\eta - (i_{01} - i_{02})\Delta x - C(d\eta/dt) \quad (5)$$

$$x_0(1-x_0)C_H(d\Delta x/dt) = -(i_{01} - i_{02})(zF/RT)\eta - (i_{01} + i_{02})\Delta x \quad (6)$$

where $\Delta x = x - x_0$.

In a previous work¹ it was found that $x_0(1-x_0)C_H \gg (RT/zF)C$.

The solution of eqns. (5) and (6) is then

$$\eta(t) = -\frac{(RT/zF)i}{(i_{01} + i_{02})} (1 - e^{-t/\tau_1}) - \frac{(RT/zF)(i_{01} - i_{02})^2 i}{4i_{01}i_{02}(i_{01} + i_{02})} (1 - e^{-t/\tau_2}) \quad (7)$$

where $\tau_1 = \frac{(RT/zF)C}{(i_{01} + i_{02})}$ and $\tau_2 = \frac{(i_{01} + i_{02})x_0(1-x_0)C_H}{4i_{01}i_{02}}$

The relation between τ_2 and τ_1 is

$$\tau_2/\tau_1 = \frac{x_0(1-x_0)C_H}{(RT/zF)C} \times \frac{(i_{01} + i_{02})^2}{4i_{01}i_{02}}$$

Since $x_0(1-x_0)C_H \gg (RT/zF)C$ and $\frac{(i_{01} + i_{02})^2}{4i_{01}i_{02}} > 1$

it follows that $\tau_2 \gg \tau_1$

In the time period where $t \ll \tau_2$, eqn. (7) simplifies to

$$\eta(t) = -\frac{(RT/zF)i}{(i_{01} + i_{02})} (1 - e^{-t/\tau_1}) - \frac{(RT/zF)(i_{01} - i_{02})^2 it}{x_0(1-x_0)C_H(i_{01} + i_{02})^2} \quad (8)$$

Eqn. (8) describes the initial growth of the overvoltage at constant current, i .

Since $x_0 = n_H/n_a$ and $C_H = en_a$, $x_0C_H = en_H$

where n_H is the number of adsorbed hydrogen atoms in the equilibrium state, and n_a is the total number of active sites on the electrode surface.

$e = 1.6 \times 10^{-19}$ coulomb.

For $x_0 \ll 1$ and $i_{01} > i_{02}$ (cf. Ref. 1), eqn. (8) can be written

$$\eta(t) = -\frac{(RT/zF)i}{(i_{01} + i_{02})} (1 - e^{-t/\tau_1}) - \frac{(RT/zF)it}{en_H} \quad (9)$$

From the experimentally obtained voltage build-up curve, $i_{01} + i_{02}$, C , τ_1 and n_H can be found.

The roughness factor. In the equations, the quantities i_{01} , i_{02} , C , C_H , and n_H are expressed in their respective units per unit real area of the electrode. If, however, the experimentally measured current is measured in amps per apparent cm² of the electrode surface, we have to introduce a roughness factor in the equations. The roughness factor f is defined as the ratio of the real to the apparent area of the electrode surface. If we introduce i/f instead of i in eqn. (9), this equation will take the form

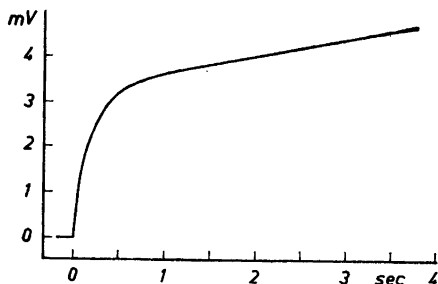


Fig. 1. The increase of the electrode potential from the open circuit potential at a constant current of $16 \mu\text{A}/\text{cm}^2$. The following data were obtained from this curve: $\bar{i}_0 = 124 \mu\text{A}/\text{cm}^2$, $fC = 910 \mu\text{F}/\text{cm}^2$, $\tau_1 = 0.18 \text{ sec}$, and $fn_{\text{H}} = 0.67 \times 10^{16}$.

$$\eta(t) = -\frac{(RT/zF)i}{(\bar{i}_{01} + \bar{i}_{02})} (1 - e^{-t/\tau_1}) - \frac{(RT/zF)it}{efn_{\text{H}}} \quad (10)$$

where

$$\tau_1 = \frac{(RT/zF)C}{(\bar{i}_{01} + \bar{i}_{02})} = \frac{(RT/zF)fC}{(\bar{i}_{01} + \bar{i}_{02})}$$

i is now expressed in amps/apparent cm^2 .

Eqn. (10) describes the initial growth of the overvoltage for all electrodes within a group of electrodes of the same nature, but with different roughness factors. The quantities that can be measured experimentally are then $\bar{i}_{01} + \bar{i}_{02}$, fC , τ_1 and fn_{H} . The time constant τ_1 is common for all electrodes within the group.

RESULTS AND DISCUSSION

Voltage transients were obtained at five different current densities for each electrode. In Fig. 1 is shown an experimental voltage build-up curve. The fast exponential rise up to a quasi-stable state is followed by a slow linear change. The results of the measurements are tabulated in Tables 1 and 2.

\bar{i}_0 = the total exchange current density ($i_0 = i_{01} + i_{02}$)

fC = the differential capacity

τ_1 = the time constant for the initial voltage build-up curve

fn_{H} = the number of adsorbed hydrogen atoms in the equilibrium state

All these quantities are then measured in their respective units per apparent cm^2 .

Table 1. Group I electrodes. Plating time = 50 sec.

Electrode No.	Plating current mA/cm^2	\bar{i}_0 $\mu\text{A}/\text{cm}^2$	fC $\mu\text{F}/\text{cm}^2$	τ_1 sec	n_{H} number/ cm^2
1	40	(42)	—	(0.37)	0.19×10^{16}
2	60	72	600	0.20	0.38
3	80	103	770	0.18	0.48
4	100	124	910	0.18	0.67
5	120	140	1050	0.18	0.81
6	140	146	1160	0.19	0.95
7	160	148	1230	0.20	1.13
8	180	182	1290	0.17	1.14
9	200	211	1400	0.16	1.47
10	220	256	1600	0.15	1.42

Table 2. Group II electrodes. Plating current = 100 mA/cm².

Electrode No.	Plating time sec	$f i_0$ $\mu\text{A}/\text{cm}^2$	fC $\mu\text{F}/\text{cm}^2$	τ_1 sec	n_{H} number/cm ²
11	10	(26)	—	(0.35)	0.15×10^{16}
12	20	27	200	0.18	0.17
13	30	64	480	0.18	0.42
14	40	76	570	0.18	0.51
15	50	90	600	0.16	0.61
16	60	130	810	0.15	0.85
17	70	118	980	0.20	0.75
18	80	136	1130	0.20	0.96
19	90	184	1150	0.15	1.14
20	100	194	1210	0.15	1.25
21	110	177	1330	0.18	1.30
22	120	182	1370	0.18	1.40

The values for electrodes Nos. 1 and 11 (the electrodes with the smallest amount of deposit) are uncertain, because the voltage/time curves obtained for these electrodes differ from the typical voltage/time curve showed in Fig. 1.

The time constant, τ_1 , is given by the ratio of the differential capacity to the total exchange current [$\tau_1 = (RT/zF)C/(i_{01} + i_{02})$], and is independent of the roughness factor or the area. It is unlikely that the exchange current and the differential capacity are dependent on the nature of the electrode in the same way, and the time constant is therefore dependent on the nature of the catalytic active sites on the electrode surface. As the time constant is measured to be nearly the same for all electrodes, it can be concluded that any electrode within the group possesses the same kind of catalytic active sites with respect to the discharge reactions.

Acknowledgement. This work was supported by the *Royal Norwegian Council for Scientific and Industrial Research*.

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Received August 29, 1963.