

Transition from Hydrogen Evolution to Oxygen Evolution on a Black Nickel Electrode

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The anodic oxidation of black nickel electrodes in 1 N KOH solution has been studied by a galvanostatic technique. The voltage/time curves at constant anodic current exhibit at least three separate regions, the voltage plateaus observed correspond to the formation of Ni(OH)_2 , NiOOH and the evolution of oxygen. Determinations of the number of coulombs consumed in each region have been made, and the true surface area is estimated from measurements in the hydrogen evolution region.

It is found that only a fraction of the surface is covered with Ni(OH)_2 before a further oxidation takes place, and that oxygen evolution begins before the build-up of a monolayer of oxide is completed.

In previously presented work,^{1,2} cathodic charging curves have been used to determine the number of hydrogen atoms adsorbed on the surface of a black nickel electrode at the equilibrium state for the hydrogen evolution reaction. The roughness-factor was estimated from measurements of the double-layer capacity, and the degree of coverage with atomic hydrogen could then be found. There is, however, a great need for an improved determination of the true surface area and the roughness-factor.

Anodic charging curves have been used for the determination of the true surface area of platinum electrodes,^{3,4} where a monolayer of adsorbed oxygen atoms is formed on the surface before oxygen evolution sets in. On nickel, the transition from hydrogen ionization to oxygen evolution proceeds through consecutive oxidation steps,⁵ and an investigation of the details of the anodic oxidation reactions is necessary before any reliable determination of the true surface area from anodic charging curves can be made.

The scope of the work presented in this paper is to investigate the possibility of determining the true surface area of black nickel electrodes from anodic charging curves.

EXPERIMENTAL

The preparation of black nickel electrodes is previously described.^{1,2} Both the cathodic and the anodic charging of the electrodes were carried out in hydrogen-saturated 1 N KOH at a temperature of 20°C. Details of the electrolytic cell and the preparation of experiments are previously described.^{1,2}

Cathodic charging. After a cathodic polarization of the test electrode, the current was interrupted, and it was confirmed that the open-circuit electrode potential attained the value of a reversible hydrogen electrode. Starting with the open-circuit potential, the build-up of overvoltage at constant current was recorded by means of an oscilloscope and photographed. Measurements were made in the current range 20–40 $\mu\text{A}/\text{cm}^2$.

Anodic charging. The test electrode was polarized cathodically before each run, and after interruption of the current the electrode potential was allowed to reach its steady state value at open-circuit. The anodic current was then switched on, and the galvanostatic voltage transients recorded and photographed. Measurements were made at the currents 1, 10, 100, and 1000 mA/cm^2 .

RESULTS AND DISCUSSION

Cathodic charging curves

In Fig. 1 is shown a typical overvoltage build-up curve at constant current. The initial build-up to a quasi-stationary value is assumed to be controlled

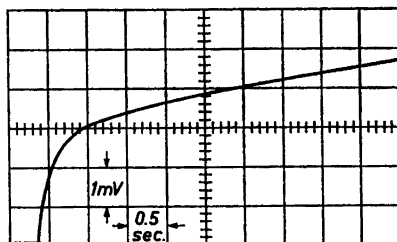


Fig. 1. Cathodic charging curve at constant current. $i_c = 30 \mu\text{A}/\text{apparent cm}^2$.

by the discharge reaction and the charging of the double layer capacitor. With increasing time, atomic hydrogen is accumulated on the electrode surface, which results in an increasing “concentration” overvoltage.

In a previous paper² it is shown that for $\eta < 5 \text{ mV}$, the following equation can be used for the first time period where the evolution of hydrogen can be neglected:

$$\eta(t) = - \frac{(RT/zF)i}{i_0} (1 - e^{-t/\tau}) - \frac{(RT/zF)it}{en_h} \quad (1)$$

$$\text{where } \tau = \frac{(RT/zF)C}{i_0}$$

i_0 = the exchange current density for the discharge reaction

C = the differential capacity

en_h = the number of coulombs corresponding to the number of hydrogen atoms, n_h , adsorbed at the equilibrium state for the hydrogen evolution reaction. $e = 1.6 \times 10^{-19}$ coulomb

$RT/zF = 25 \text{ mV}$ at 20°C

Table 1. Values of the roughness-factor, and the degree of coverage with adsorbed hydrogen for black nickel hydrogen electrodes in hydrogensaturated 1 N KOH.

Electrode No.	en_h mC/apparent cm ²	f	en_h/f mC/cm ²	x_0
1	2.27	120	0.019	0.059
2	1.72	94	0.018	0.056
3	1.56	106	0.015	0.047
4	1.69	113	0.015	0.047
5	1.56	102	0.015	0.047
6	1.92	115	0.017	0.053
7	1.72	107	0.016	0.050
8	2.17	123	0.018	0.056
9	2.00	131	0.015	0.047
10	1.96	120	0.016	0.050

The roughness-factor. The roughness-factor, f , is given by the relation $f = C/C_0$, where $C_0 = 16\mu\text{F}/\text{cm}^2$ (the capacity of a Hg electrode under cathodic polarization).

Degree of coverage. The charge corresponding to a monolayer of atomic hydrogen, assuming a 1:1 H:Ni ratio is approximately 0.32 mC/cm². For an electrode with roughness-factor f , the charge is $0.32f$ (mC/apparent cm²). The degree of coverage is therefore given by:

$$x_0 = en_h/0.32f$$

The experimental values of en_h are tabulated in Table 1, together with the calculated values of f and x_0 .

Anodic charging curves

The anodic oxidation of single crystals of nickel in 0.2 N KOH has been studied at controlled potential by Weininger and Breiter.⁵ They discussed their results with regard to the following mechanism:

At *ca.* 0.4 volt *vs.* a reversible hydrogen electrode in the same solution, Ni(OH)₂ is formed, according to



The oxyhydroxide NiOOH is produced at *ca.* 1.4 volt



At still higher potentials oxygen is evolved.

Characteristic features of the anodic charging curves. In Fig. 2 are shown galvanostatic charging curves obtained on a black nickel electrode in hydrogen-saturated 1 N KOH at anodic c.d.s of 1–10 and 100 mA/apparent cm². There are three voltage-plateaus corresponding to the current peaks obtained at controlled potential.⁵ The charging curves may be divided into four regions:

- The hydrogen ionization region (0 to 0.39 V).
- The region representing the formation of Ni(OH)₂ (0.39 to 1.38 V).
- The region representing the oxidation to NiOOH (1.38 to 1.78 V).
- The oxygen evolution region (starts at 1.78 V).

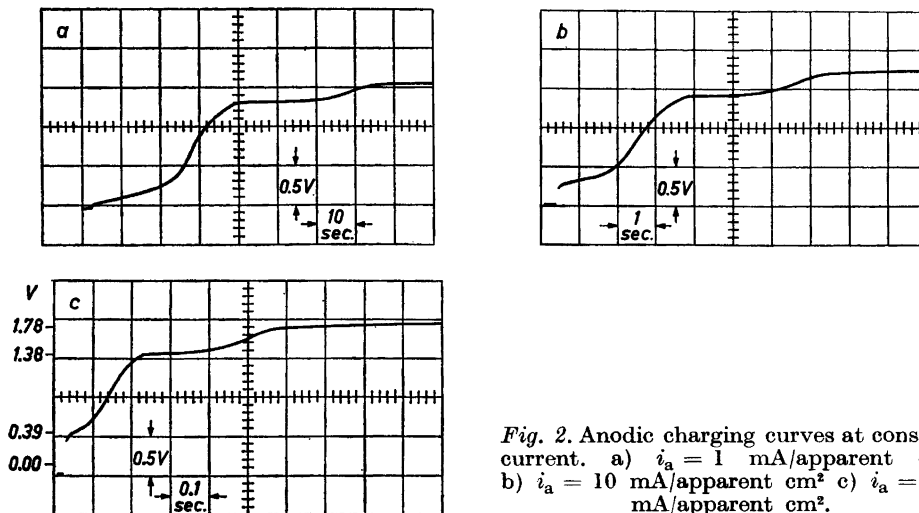


Fig. 2. Anodic charging curves at constant current. a) $i_a = 1$ mA/apparent cm^2 . b) $i_a = 10$ mA/apparent cm^2 c) $i_a = 100$ mA/apparent cm^2 .

At the lowest c.d., diffusion of molecular hydrogen towards the electrode surface sustains the hydrogen ionization reaction. This is reflected in the voltage/time curve (Fig. 2a). At 100 mA/ cm^2 , however, the limiting diffusion current is negligible, and the first step in the voltage/time curve from zero up to 0.39 V is controlled by the ionization of the absorbed hydrogen atoms and the charging of the double layer capacitor.

Charge measurements. The number of coulombs consumed in each region was determined in the following way. Since the current was constant, the charges could be obtained by multiplying the measured transition time of each region by the applied current.

An interesting conclusion which can be drawn from an inspection of charging curves at different c.d.'s is that the number of coulombs consumed in region C is independent of the current (*cf.* Table 2).

The result of charge measurements in the regions where the oxide layers are formed (B and C) are tabulated in Table 3. The measured values are given in millicoulombs per unit geometrical area. In order to convert these data into mC per unit true surface area, the values are divided by the roughness-factor tabulated in Table 1.

Degree of coverage. The charge required to build up a monolayer of $\text{Ni}(\text{OH})_2$ on 1 cm^2 of Ni is *ca.* 0.6 mC, and *ca.* 0.3 mC is required to the continued oxidation of $\text{Ni}(\text{OH})_2$ to NiOOH . A part of the supplied charge is also consumed by the double layer capacitor. It can therefore be concluded from the data of Table 3 that only a small fraction of the electrode surface is covered with

Table 2. Number of coulombs consumed in region C (1.38 to 1.78 V) at different current densities.

Charge measurements,	mC/ cm^2	34	35	33	32
Current density,	mA/ cm^2	1	10	100	1000

Table 3. Charges required to form the oxide layers on the electrodes during anodic charging at 100 mA/cm².

Electrode No.		1	2	3	4	5	6	7	8	9	10
mC/cm ² of apparent surface area	B	20	15	15	17	16	17	14	18	19	18
	C	34	30	30	33	34	31	31	33	33	31
mC/cm ² of true surface area	B	0.17	0.16	0.14	0.15	0.16	0.15	0.13	0.15	0.15	0.16
	C	0.28	0.32	0.28	0.29	0.33	0.27	0.29	0.27	0.25	0.26

Ni(OH)₂ before a further oxidation takes place, and that oxygen evolution begins before the build-up of a monolayer of NiOOH is completed.

SUMMARY

- When black nickel electrodes in hydrogen saturated 1 N KOH solution are anodically polarized at constant current (c. d. range, 1→1000 mA/apparent cm²), charge is consumed in the following processes.
 - Ionization of absorbed hydrogen atoms.
 - Oxidation of Ni to Ni(OH)₂. Begins at *ca.* 0.39 V *vs.* a hydrogen reference electrode.
 - Oxidation of Ni(OH)₂ to NiOOH. Begins at *ca.* 1.38 V *vs.* HRE.
 - Oxygen evolution. Begins at *ca.* 1.78 V *vs.* HRE.
 - Charging of the double layer capacitor.
- Only a fraction of the electrode surface is covered with oxidized substance before the next oxidation step sets in. The method used for the determination of the true surface area of a platinum electrode can therefore not be used for nickel electrodes.
- Within the applied c.d. range, the charge consumed by the reaction Ni(OH)₂ + OH⁻ = NiOOH + H₂O + e⁻ is independent of the current supplied to the electrode. This fact makes it possible to compare true surface areas of electrodes of the same kind, and thereby determine the relative roughness-factors between electrodes.

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