

# The Catalytic Properties of Black Nickel Hydrogen Electrodes

## Part. II. The Surface Roughness and the Hydrogen Overvoltage on Black Nickel Electrodes

ODD RIISØEN

*Cr. Michelsen Institute, Dept. of Applied Physics, Bergen, Norway*

The behaviour of black nickel hydrogen electrodes with different grades of surface roughness has been studied at high current densities. Steady state overvoltage measurements are made in the current density range  $10^{-4}$  to  $10^{-1}$  A/apparent  $\text{cm}^2$ , and the double layer capacity at constant overvoltage is measured by a current step method. From the results of the capacity measurements, the relative roughness factor is estimated for each individual electrode.

In order to study the behaviour of all electrodes at the same true current density (current per unit real area of the electrode surface), the overvoltage has been plotted as a function of  $i/f$ , where  $i$  is the apparent current density and  $f$  the relative roughness factor for the electrode. It is found that the Tafel lines, drawn on the basis of the true current density, are nearly identical, indicating that the electrodes differ only in their effective area, and that they possess the same kind of catalytic active sites with respect to the over-all hydrogen evolution reaction.

It is evident from the results presented in the literature concerning overvoltage measurements on nickel cathodes, that the activity of nickel electrodes with respect to the hydrogen evolution reaction is very much dependent on the preparation of the electrode surface. Makrides and Coltharp<sup>2</sup> prepared nickel electrodes having an activity (*i.e.* current density for a given overvoltage) about 40 times that of the nickel electrodes of Bockris and Potter,<sup>3</sup> and electro-deposited nickel electrodes about 400 times as active as those of Bockris and Potter have been reported by Peers.<sup>4</sup>

In this paper we present the result of overvoltage and roughness factor measurements on a group of black nickel electrodes. In a previous investigation,<sup>1</sup> the behaviour of black nickel electrodes in 1 N KOH solution has been studied in the vicinity of the equilibrium state for the hydrogen evolution reaction. It was found that the double layer capacity per unit area and the exchange current density for the proton discharge reaction were constants

characteristic for the whole group of electrodes if these quantities were based on the real area of the electrode surface.

### EXPERIMENTAL

The preparation of electrodes and the experimental procedure have been described previously.<sup>1</sup> The experiments were carried out on a number of black nickel electrodes plated as described for the electrodes in group II.<sup>1</sup> The electrode potential was measured against a black platinum hydrogen electrode, and the build-up of voltage at constant current was followed on a medium speed recorder at a paper speed of 5 mm/sec. At overvoltage values more negative than  $-100$  mV, a steady state was reached within a few seconds. Between the measurements the current was interrupted, and the potential was allowed to reach its steady state rest potential.

The double layer capacity at a given overvoltage was measured by a current step method. Small current steps from a fast pulse generator were superposed the steady state current, and the voltage transients were displayed on an oscilloscope and photographed.

### THEORETICAL BASIS FOR THE CAPACITY MEASUREMENTS

There is much experimental evidence indicating that the rate determining reaction is either the discharge reaction or the electrochemical reaction.<sup>5</sup> At potentials far from the equilibrium potential, the voltage/current relation has then the form of the Tafel equation. If we use the European convention of signs for electrode potentials, and the convention of regarding a net cathodic current as positive

$$\eta = a - b \ln i_r \quad (1)$$

where  $\eta$  is the overvoltage,  $i_r$  the reaction current and  $a$  and  $b$  are constants. The capacitive current is given by

$$i_c = -C(d\eta/dt) \quad (2)$$

where  $C$  is the capacity of the double layer.

The externally measured current is the sum of the reaction current and the capacitive current

$$i = i_c + i_r \quad (3)$$

For small changes in  $\eta$  and  $i$  about a steady state operating point, we can use the linear equations

$$\Delta\eta = -(b/i) \Delta i_r \quad (4)$$

$$\Delta i_c = -C(d\Delta\eta/dt) \quad (5)$$

$$\Delta i = \Delta i_c + \Delta i_r = -(i/b) \Delta\eta - C(d\Delta\eta/dt) \quad (6)$$

If  $\Delta i$  is a step function, the change in  $\eta$  with time is given by

$$\Delta\eta = -(b/i) \Delta i_s (1 - e^{-t/\tau}) = \Delta\eta_s (1 - e^{-t/\tau}) \quad (7)$$

where  $\tau = C(b/i) = C(-\Delta\eta_s/\Delta i_s)$ , and the new steady state is  $(i + \Delta i_s)$ ,  $(\eta + \Delta\eta_s)$  as  $t \rightarrow \infty$ .

Experimentally,  $\Delta\eta_s$  and  $\tau$  can be found from an examination of the voltage/time curve, and  $C$  can then be calculated from  $C = (\Delta i_s / -\Delta\eta_s) \tau$ .

Table 1. The double layer capacity, measured in the overvoltage range  $-100$  to  $-250$  mV. Group II electrodes. Plating current  $100$  mA/cm<sup>2</sup>.

Electrode No.	1	2	3	4	5	6	7	8	9	10	11
Plating time(sec)	10	20	30	40	50	60	70	80	90	100	110
$C$ ( $\mu\text{F}/\text{cm}^2$ )	85	115	190	220	280	300	300	320	340	400	470
$f = C/C_5$	0.30	0.41	0.68	0.79	1.00	1.07	1.07	1.14	1.21	1.43	1.68

## RESULTS

*The roughness factor.* At electrode potentials where the steady state voltage/current relation is represented by a straight Tafel line, the capacity had its minimum value and did not vary with voltage in the overvoltage range from about  $-100$  to  $-250$  mV. In Table 1 is tabulated the results of capacity measurements on the group of electrodes examined.

As we do not know the capacity per unit real area for black nickel electrodes operating at the given conditions, the absolute value of the roughness factor cannot be determined by the capacity measurements alone. We therefore use electrode No. 5 as a standard, and define the relative roughness factor for an electrode as the ratio of the real area of this electrode to the real area of electrode No. 5. We assume that the relative roughness factor for an electrode with capacity  $C$  can be found from  $f = C/C_5$ .  $C_5$  is the capacity measured on electrode No. 5. The relative roughness factors are listed in Table 1.

*Tafel lines.* Fig. 1 shows the result of steady state overvoltage/current measurements on electrodes with different roughness factors. The current density,  $i$ , is here the apparent current density, and is expressed in amps per apparent cm<sup>2</sup>. Owing to the differences in surface roughness, the curves are widely spread.

In order to compare the behaviour of the electrodes, the overvoltage must evidently be referred to the same true current density. In Fig. 2 are shown the limits for the Tafel lines when the overvoltage is plotted against  $\log(i/f)$ , where  $f$  is the relative roughness factor for each individual electrode. The Tafel lines for all examined electrodes (11 electrodes) lie within the shaded area.

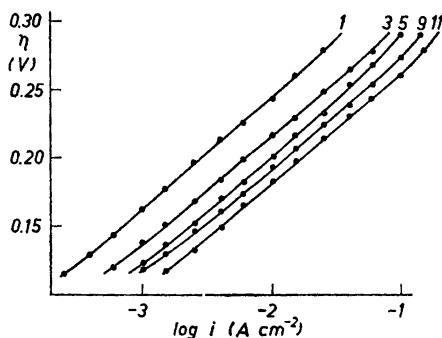


Fig. 1. Tafel lines for 5 different electrodes within the group of black nickel electrodes.  $i$  is expressed in A/apparent cm<sup>2</sup>.

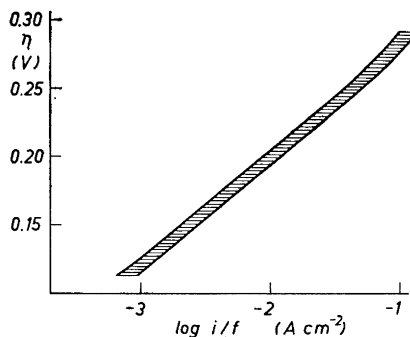


Fig. 2. The limits for the normalized Tafel lines.

### CONCLUSIONS

If examined at the same true current density, the electrodes within the group of black nickel electrodes showed very small variations in properties. An individual electrode within the group can then be characterized by properties common for the whole group, and the specific roughness factor for that electrode.

This conformity in properties for black nickel electrodes is in contrast to the very great variation in properties for "smooth" nickel electrodes. Very differing results are reported in the literature concerning overvoltage measurements on "smooth" nickel electrodes with apparently the same surface roughness, and operating at equivalent conditions in the electrolytic cell.

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

### REFERENCES

1. Riisøen, O. Part I of this publication. *Acta Chem. Scand.* **17** (1963) 2600.
2. Makrides, A. C. and Coltharp, M. T. *J. Electrochem. Soc.* **107** (1960) 472.
3. Bockris, J. O' M. and Potter, E. C. *J. Chem. Phys.* **20** (1952) 614.
4. Peers, A. M. *J. Electrochem. Soc.* **108** (1961) 603.
5. Riisøen, O. *Acta Chem. Scand.* **17** (1963) 657.

Received August 29, 1963.