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Conference Paper

Oxidation on the Nickel Hydroxide Electrode*

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It has been shown that in alkaline solution alcoholic hydroxyl is oxidized by the charged nickel hydroxide electrode — similarly as by oxidation in the presence of nickel salt catalysts or by »nickel peroxide« — to carboxylic acid.

An electrochemical method has been devised for the study of the reaction rate, based on the potentiometric indication of the depletion of NiOOH. It has been shown that the reaction rate is proportional to the amount of NiOOH and the concentration of the alcohol, but independent of the hydroxide ion concentration and the electrode potential.

An electrochemical procedure has been devised for the practical implementation of oxidation on NiOOH. In this way a number of primary alcohols may be oxidized with good yields. It has been shown that the oxidation of the vitamin C intermediate di-*O*-isopropylidene-sorbose can be performed electrochemically with yields above 95% and, according to estimates, economically on an industrial scale.

According to literature, oxidation in alkaline media generally causes serious difficulties; there arise problems of electrode stability on the one hand, while on the other the reaction is difficult to controle; frequently different products result simultaneously and in some cases condensation products too. The NiOOH electrode has been extensively employed and studied by electrochemists in the past decades. From our investigation it can be concluded that on the nickel hydroxide electrode the oxidation of alcohols, aldehydes *etc.* can be carried out.

EXPERIMENTAL

Nickel hydroxide electrodes can be prepared by exposing a carefully cleaned nickel or platinum sheet to alternate anodic and cathodic polarization in a solution of 0.1 *N* $NiSO_4$, 0.1 *N* CH_3COONa and 0.005 *N* NaOH[1]. By this procedure nickel hydroxide equivalent to a charge ranging from a few mcoulomb/cm^2 to a few hundred mcoulomb/cm^2 was deposited on the electrode, the actual amount depending on the current intensity and the duration of the polarization. The layer thus formed was subsequently charged in a pure alkaline solution, whereupon a black layer, resembling platinized platinum, appeared on the electrode. (Very thin layers are of a pale violet colour.) In the process current densities of 10 A/cm^2 to 1 mA/cm^2 can be employed.

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Investigations on the nickel hydroxide electrode were carried out in a conventional three-compartment cell. All three compartments, communicating through ungreased ground glass joints, were filled with *N* NaOH solution. The central compartment held the nickel hydroxide electrode and the solution of the compound to be oxidized. Occasional gas bubbles sticking to the electrode surface were removed by gently stirring the solution by a magnetic stirrer (500 r. p. m.). One of the side compartments contained the polarizing auxiliary electrode, and the other the reference electrode for potential measurement, connected to the central compartment by a Luggin-capillary. As reference electrode, a platinized platinum electrode was used flushed by purified hydrogen. Accordingly, potential values given in the paper always refer to a hydrogen electrode of 1 atm in the same solution as the one surrounding the main electrode. The cell was provided with a glass jacket through which water of 25.0 ± 0.1 °C temperature was circulated by an ultrathermostat.

The preparation of carboxylic acids was carried out in a different type of apparatus, consisting of a cylindrical nickel hydroxide electrode of about 2 dm^2 surface, prepared by the above procedure, inserted into a 400 ml beaker, in a way that the electrode should fit the wall of the beaker. In the oxidation of alcohols anode and cathode spaces need not be separated (*i. e.* there is no need for a diaphragm), since carboxylic acids formed are not reduced at the cathode. As to the quality of the cathode, there are no special requirements, except that it should not be corroded under the experimental conditions. So a graphite rod cathode of about 1 cm diameter was placed in symmetrical arrangement with respect to the nickel hydroxide anode. Under laboratory conditions current may be provided by a battery-charger.

The Rate Equation of Oxidation

The charged nickel hydroxide electrode may be discharged not only by current. So, *e. g.* if a charged nickel hydroxide electrode is immersed into a *N* KOH solution containing 2.5 mole/l of ethanol, a change in the potential, shown in Fig. 1, can be observed. Discharge curves, with respect to other substrates, are shown in Fig. 2.

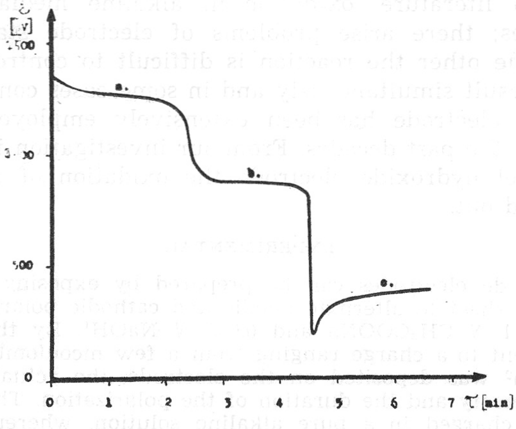

Fig. 1. Change of potential of NiOOH electrode in ethanol solution.

It is obvious from the run of the curves that a reaction has taken place between the electrode and the solution, moreover that the electrode has been reduced.

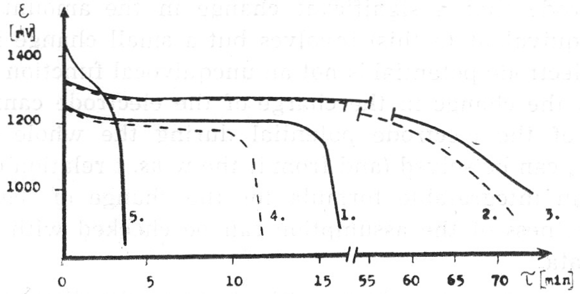

Fig. 2. Oxidation of various compounds by NiOOH electrode in *N* KOH solution on a Pt-sheet of 10 cm² surface area.
1. 2 mole/l propanol, *2.* 1 mole/l butanol, *3.* 1 mole/l pentanol, *4.* 0.02 mole/l allyl alcohol, *5.* 0.03 mole/l formaldehyde.

In the case of electrochemical oxidation the transformation of the nickel hydroxide can be followed by recording the electrode potential. Thus, *e. g.* the curve in Fig. 1 has three horizontal regions, each of which corresponds to a reaction. At the end of region a the potential drops below 1000 mV, indicating that NiOOH cannot be present on the electrode. This conclusion is further supported by the fact that the potential interval corresponding to this arrest coincides with that of the first horizontal arrest of the discharge curve measured when discharging the electrode by current. For the time being, the origin of region b is unknown. On discharging by current, this region appears at very low current densities, and is assumed to be due to a reduction of some nickel oxide or of oxygen adsorbed on $Ni(OH)_2$. In the present case it can be attributed to a similar, by all means slow, reaction. Due to this uncertainty, in the course of further work the appearance of this section was avoided by the proper choice of conditions. The position and shape of section c are determined by the oxidation-reduction properties of the compound studied, in the present case ethanol.

By definition the rate of reaction

$$NiOOH + \text{organic compound} \rightarrow Ni(OH)_2 + \text{intermediate}$$

is

$$w = -\frac{dQ}{dt} \tag{1}$$

where Q is the amount of NiOOH on the electrode at time t. If the electrode is polarized cathodically with a given current I simultaneously with the discharge by added substrate[2,3] Eq. (1) is modified as follows

$$-\frac{dQ}{dt} = w + I \tag{2}$$

For the determination of the instantaneous values of the reaction rate, a knowledge of the corresponding Q, t pairs is necessary during the whole reaction time. From the measurements merely the change of the electrode potential with time (the ε *vs.* t relation) is known. It may be seen from the discharge curves determined from measurements in pure alkali solution on a NiOOH electrode that a significant change in the amount of NiOOH (or of the charge equivalent to this) involves but a small change in the electrode potential. The electrode potential is not an unequivocal function of the electrode charge[4-14]. Thus the change in the charge of the electrode cannot be followed with the help of the electrode potential during the whole discharge time. Eq. (2), however, can be solved (and from it the w *vs.* t relation can be obtained) if we assume an integratable formula for the change of reaction rate with time. The correctness of the assumption can be checked with the help of the experimental data.

We can assume for example that (similarly to the discharge with electric current) the reaction rate is constant during the whole discharge time, then solving Eq. (2) we have

$$Q = Q_0 - (w + I)\, t_r \qquad (3)$$

where t_r is the total time elapsed from the beginning of discharge with current and substrate. From simple experiments[2,3] it follows that the assumption of constant reaction rate is inncorrect.

An other assumption is

$$w = k \cdot Q \qquad (4)$$

where k is a constant. By substituting this relation into Eq. (2) and integrating under boundary condition $Q = Q_0$ at $t_r = 0$ and $Q = 0$ at $t_r = t_*^{I}$ (Fig. 3)

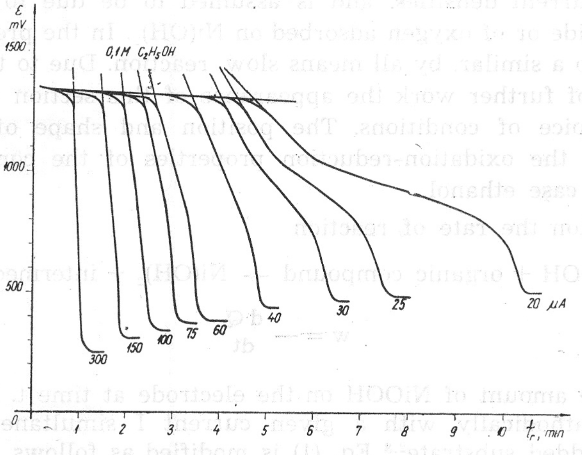

Fig. 3. Discharge curves of NiOOH electrode ($Q_0 = 26$ mC) in 0.1 *M* ethanol with additional cathodic polarization. Time of complete discharge (t_r*) for given current

I μA	300	150	100	75	60	40	30	25	20
t_r* sec	50	88	113	141	156	204	240	258	282

$$\frac{I}{I + k \cdot Q_0} = e^{-kt_r^*} \qquad (5)$$

Using Eq. (5) the proportionality factor k can be calculated from the duration of the potential plateaus of the discharge curves in the case of a given concentration with different currents. The method of constant differences may be used in the calculation. If

$$\Delta t_r^* = t_{r_2}^* - t_{r_1}^* \tag{6}$$

is constant and

$$e^{k\Delta t_r} = A, \tag{7}$$

we obtain

$$\frac{1}{I_2} = \frac{A-1}{k\,Q_0} + A\,\frac{1}{I_1} \tag{8}$$

At current strength I_2 the discharge time is greater by exactly Δt_r^* than the discharge time observed at I_1. Plotting $1/I_1$ against $1/I_2$, according to the assumption, a straight line must be obtained. From the slope of this, using Eq. (7), the value of k can be calculated.

It may be seen in Fig. 4 that the points give a straight line to a good approximation. In this way Eq. (4) proved to be the correct initial assumption,

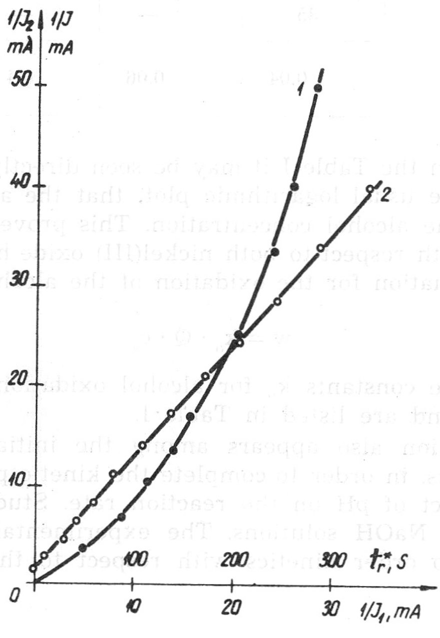

Fig. 4. Oxidation of 0.1 *M* ethanol on a NiOOH electrode.
1. $1/I - t_r^*$ relation.
2. $1/I_2 - 1/I_1$ transformation on the basis of Eq. (8). $\Delta t_r^* = 20$ sec.

and this also means that Eq. (4) does indeed describe the rate of oxidation of ethanol (and on the basis of other findings, of other primary alcohols) on a nickel hydroxide electrode. The relation shows that the rate of oxidation during the complete time of reaction is proportional to the amount of nickel(III) oxide hydroxide on the electrode. Thus the constant k may be considered as an apparent rate constant because it is the proportionality factor in the relationship connecting the reaction rate and the instantaneous amount of one of the reactants.

The effect of alcohol concentration on the rate of oxidation on the nickel hydroxide electrode was studied in detail for methanol and ethanol. We determined for each alcohol the value of the apparent rate constant k in alcohol solutions of different concentrations. The values calculated from the results are given in Table I.

TABLE I

Rate Constants of the Oxidation of Alcohols on Nickel Hydroxide at 25.0° C

Alcohol concentration *M*	Apparent rate constant, $k \times 10^{-3}$ (sec^{-1})			
	Methanol	Ethanol	Benzyl alcohol	Furfuryl alcohol
0.01	—	0.6	3.9	7.8
0.03	1.0	1.8	—	—
0.10	3.5	6	45	—
0.30	12	17	—	
1.00	35	—	—	
k_0 $M^{-1} \times sec^{-1}$	0.04	0.06	0.4	0.8

From the data in the Table I it may be seen directly, and may be proved beyond doubt by the usual logarithmic plot, that the apparent rate constant is proportional to the alcohol concentration. This proves that the reaction is of the first order with respect to both nickel(III) oxide hydroxide and alcohol. That is, the rate equation for the oxidation of the alcohol is of the following form:

$$w = k_0 \cdot Q \cdot c_a \tag{9}$$

Accordingly, the rate constants k_0 for alcohol oxidation on nickel hydroxide can be calculated, and are listed in Table I.

The hydroxide ion also appears among the initial components of the overall reaction. Thus, in order to complete the kinetic picture, it is necessary to examine the effect of *p*H on the reaction rate. Studies were made using 0.01, 0.1 and 1.0 *N* NaOH solutions. The experimental results are in good agreement with zero order kinetics with respect to the hydroxide ion concentration.

Electrochemical Oxidation of Alcohols

Regarding the variety of oxidation processes that can be carried out on nickel hydroxide powder[15], the use of nickel hydroxide electrode makes a number of reactions feasible by electrochemical methods, opening thereby new fields for organic electrochemistry.

In the following a few examples are given on the application of nickel hydroxide electrode.

a) The method is demonstrated in detail on the example of 2,3:4,6-di-*O*-isopropylidene-L-sorbose (DIS). DIS, being an intermediate of ascorbic acid synthesis, is a compound of industrial importance. A number of methods are known for the oxidation of DIS, which contains a single primary alcoholic hydroxyl group. The oxidants used (NaOCl, $KMnO_4$) are mostly prepared by electrolysis, therefore the economic advantages of a direct electrolytic oxidation may be significant.

The oxidation of DIS was carried out in the following way.

As starting material, industrial DIS of 90% purity was used. 300 ml of a solution of 100 g/l DIS and 35 g/l NaOH were filled into the sample cell described above, and was electrolysed for 3 hr at a current of 10 A. The temperature of the solution increased during electrolysis. Foaming at the onset of the electrolysis was, in the majority of cases not so vigorous as to cause spilling of the solution. Since foaming is caused by impurities, current density should occasionally be reduced at the outset of the electrolysis, lengthening thereby its duration.

After the end of the electrolysis the solution was cooled in an ice bath, and was acidified in the usual manner, checking the value of *p*H by an indicator strip. DIH (di-*O*-isopropylidene-L-*xylo*-hexulosonic acid monohydrate) precipitated at $pH = 3.5$—4. Experience has shown that at 0° C an acidity up to $pH = 1$ is not detrimental. The precipitate was filtered off, washed with a small amount of cold water (about 0° C), and dried at 40—50° C. Yield data obtained under different conditions of electrolysis are given in Table II.

TABLE II

Oxidation at NiOOH Electrode of 30 g of Industrial (90%) DIS at Different Current Intensities

Current A	Time hr	DIH g	Yield calculated with respect to 90% DIS
2.0	10	29.2	96
2.5	7	29	96
3.2	8	28.5	94
3.5	5	28	92
10.0	2	28	92
10.0	2.5	27.5	91
15.0	1.5	28.5	94
24.0	1.0	29	96

The above results show that current density and the duration of the electrolysis may be varied in a wide range. Current yields are, of course, very different. It is clear, however, from the results given that although a current yield of 60—70% is easily obtained, in this case the duration of the electrolysis should be relatively long (using the same cell and DIS quantity). Very probably even higher current yields could be obtained. It depends on economic considerations whether the current yield or the duration of the electrolysis is given priority. (An industrial process is disclosed in a patent of us[16]). On laboratory scale, where the primary object is a rapid preparation with a good yield, it is not worthwhile to strive for high current yield.

The following examples illustrate that the electrode can also be used for the oxidation of other alcohols. In these examples no exact procedure **is** given, and in the research work no emphasis was placed on high yields, as there are better methods for the preparation of the carboxylic acids in question.

b) A solution of 25 g of benzyl alcohol and 40 g of NaOH in 1000 ml of water was electrolysed at room temperature, at nickel hydroxide electrode, for 2 hours, with a current density of 3.5 A/dm^2. The solution was acidified and 24 g of benzoic acid were obtained.

c) A solution of 23 g of ethanol and 25 g of NaOH in 300 ml of water was electrolysed at room temperature, for 2$^1/_2$ hours, with a current density of 4 A/dm^2. The solution was acidified, and distilled. 14 g of acetic acid were obtained.

d) A solution of 22 g of *n*-amyl alcohol and of 15 g of NaOH in 300 ml of water was electrolysed at room temperature for 2$^1/_2$ hours, with a current density of 1.5 A/dm^2. The solution was acidified and destilled. 7 g of valeric acid were obtained.

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IZVOD

Oksidacije na nikal-hidroksid elektrodi

G. Vertes, G. Horányi i F. Nagy

Opisani su eksperimenti oksidacije metanola, etanola, benzil-alkohola i furfuril alkohola na nikal-hidroksid elektrodi. Pokazano je da je brzina reakcije ovisna o količini NiOOH na elektrodi i o koncentraciji alkohola u otopini, a neovisna o

koncentraciji hidroksil-iona. Dobra aktivnost nikal-hidroksid elektroda za oksidaciju alkohola otvara mogućnosti za primjenu tog tipa elektroda u industriji. Tako su u radu opisani i eksperimenti oksidacije 2,3:4,6-di-*O*-isopropiliden-L-sorboze u alkalnim otopinama (35 g/l NaOH) u produkt koji je iz kisele otopine kristaliziran kao di-*O*-isopropiliden-L-*ksilo*-heksulonska kiselina. Iskorištenja se kreću do 96%, što dozvoljava ekonomičnu proizvodnju.

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