Tetrahedron. Vol. 28, pp. 37 to 42. Pergamon Press 1972. Printed in Great Britain

A NEW METHOD FOR THE ELECTROCHEMICAL OXIDATION OF ALCOHOLS

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(*Received in the UK* 18 *May* 1971; *Accepted for publication* 24 *August* 1971)

Abstract—Considering the effect of nickel salts in catalytic oxidation processes, the results of investigations on oxidation by "nickel peroxide" as well as the electrochemical characteristics of the nickel hydroxide electrode, it can be assumed that oxidation of alcohols, aldehydes, etc. can be carried out on a charged nickel hydroxide electrode.

This assumption has been experimentally verified, and it has been shown that charged nickel hydroxide electrodes are reduced in alkaline solutions of alcohols.

In this paper practical applications of nickel hydroxide electrodes are reported, and a preparative method is proposed for the electrochemical oxidation of primary alcohols. The method is illustrated in detail on the example of di-isopropilidene-sorbose oxidation.

IN THE LAST DECADE nickel hydroxide was used for the oxidation of a number of organic compounds. Some of the processes utilize nickel hydroxide as an oxygen transferring catalyst,[1] whereas in other processes oxidation is carried out by means of previously prepared nickel peroxide.[2,3]

It is known from electrochemical studies[4] that no chemical difference can be observed between chemically prepared nickel hydroxide, and active nickel hydroxide formed on a nickel hydroxide electrode. This fact led to the assumption that the nickel hydroxide electrode can advantageously be utilized in several oxidation processes. For this purpose the behaviour of charged nickel hydroxide electrodes was studied in alkaline solutions of organic substances, (alcohols and aldehydes) and a process has been elaborated for the implementation of electrochemical oxidation.

The interaction of alcohols and the nickel hydroxide electrode

The nickel hydroxide electrode has been studied and used for decades.[6]

The discharge and charging curves taken at a constant current are shown in Fig. 2, when time τ, is proportional to the charge.

The charged nickel hydroxide electrode may, of course, be discharged not only by current. When a charged nickel hydroxide electrode is immersed into a N KOH solution containing 2·5 mole/l of EtOH, a change in the potential, (Fig. 3) can be observed. Discharge curves, with respect to other substrates, are shown in Fig. 4.

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.

In the case of electrochemical oxidation the transformation of the nickel hydroxide can be followed by recording the electrode potential. Thus, the curve in Fig. 3 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. (See section BC, Fig. 2.) 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 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 EtOH. This effect, in the case of the Pt electrode, has already been pointed out.[7]

Electrochemical oxidation of alcohols

It has been found that reactions taking place on powdered nickel hydroxide also take place on the nickel hydroxide electrode. This fact has, in our opinion, a great practical importance.

The main problem of the implementation of organic reactions by electrochemical methods is, in any particular case, the choice of a suitable electrode.

The number of practically useful types of electrodes, especially in alkaline solutions, is restricted. Regarding the variety of oxidation processes that can be carried out on nickel hydroxide powder, the use of a nickel hydroxide electrode makes a number of reactions feasible by electrochemical methods, thereby opening new fields for organic electrochemistry.

In the following a few examples are given on the application of the 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 OH 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 simple cell described below, and was electrolysed for 3 hr at a current intensity 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, thus lengthening its duration.

At the end of electrolysis the solution was cooled in an ice bath, and was acidified in the usual manner, checking the pH 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° an acidity up to pH = 1 is not detrimental. The precipitate was filtered, washed with a small amount of cold water (about 0°), and dried at 40–50°. Yield data obtained under different conditions of electrolysis are given in Table 1.

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,

TABLE 1. 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

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 ours.[8]) On a laboratory scale, where the primary object is a rapid preparation with a good yield, it is not worthwhile to strive for a 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 temp, at a nickel hydroxide electrode, for 2 hr, 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 EtOH and 25 g of NaOH in 300 ml of water was electrolysed at room temp, for 2½ hr, with a current density of 4 A/dm^2. The solution was acidified, and distilled to give AcOH (14 g).

(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 temp for 2½ hr, with a current density of 1·5 A/dm^2. The solution was acidified and distilled to give valeric acid (7 g).

EXPERIMENTAL

Nickel hydroxide electrodes can be prepared by exposing a carefully cleaned Ni or Pt 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[5]. 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 Pt, appeared on the electrode. (Very thin layers are of a pale violet colour.) In the process current densities of 10 μA/cm^2 to 1 mA/cm^2 can be employed.

Investigations on the nickel hydroxide electrode were carried out in a conventional three-compartment cell (Fig. 1). 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 one the reference electrode, for potential measurement, connected by a Luggin-capillary to the central compartment. As reference electrode, a platinized Pt

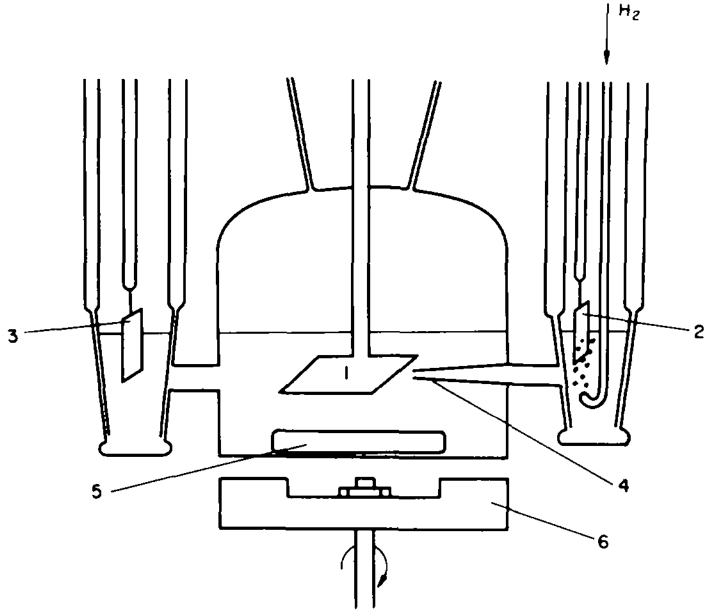

FIG 1. Experimental cell for the study of the NiOOH electrode. 1—NiOOH electrode, 2—reference electrode, 3—auxiliary electrode, 4—Luggin capillary, 5—teflon-covered magnetic rod, 6—rotating magnet.

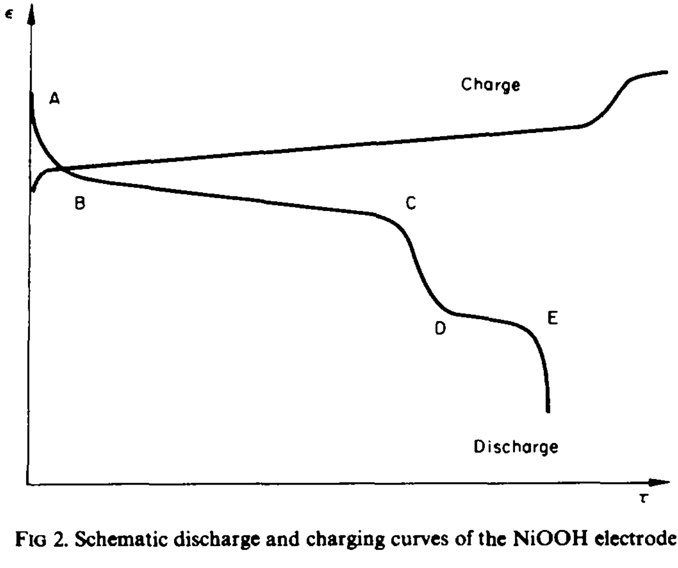

FIG 2. Schematic discharge and charging curves of the NiOOH electrode.

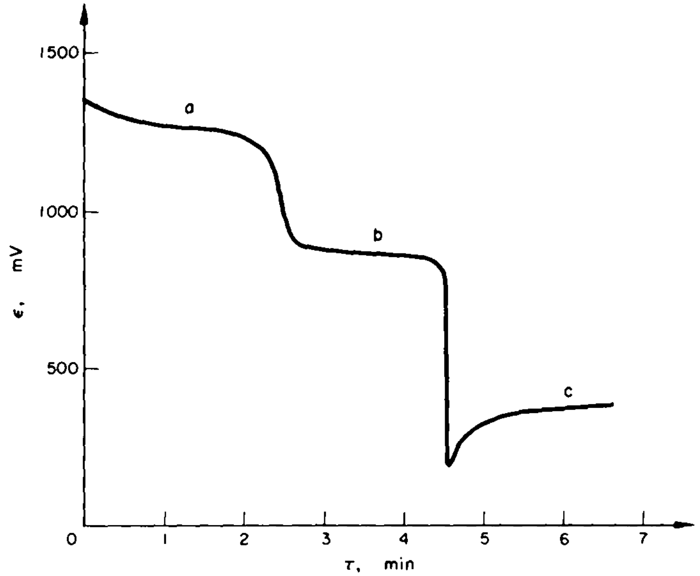

FIG 3. Change of the potential of NiOOH electrode in EtOH.

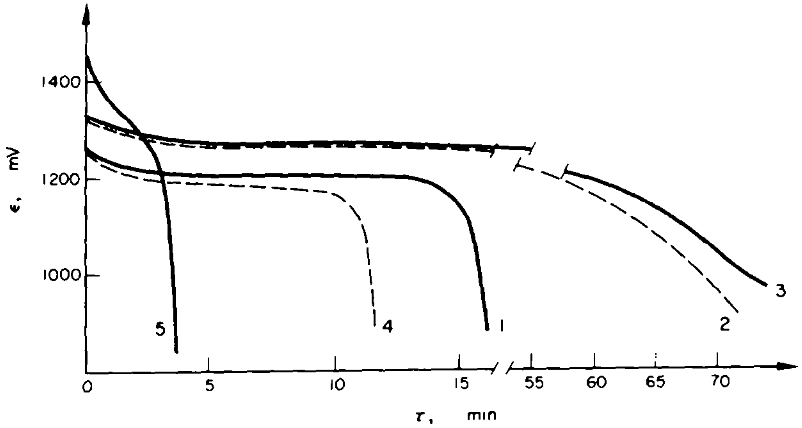

FIG 4. Oxidation of various compounds by NiOOH electrode on a Pt sheet of 10 cm^2 surface area, in N KOH solution. 1—2 mole/l propanol, 2—1 mole/l butanol, 3—1 mole/l pentanol, 4—0·02 mole/l allyl alcohol, 5—0·03 mole/l formaldehyde.

electrode of about 2 cm^2 apparent surface area was used and 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° 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 such a way that the electrode fitted 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 a symmetrical arrangement with respect to the nickel hydroxide anode. Under laboratory conditions current may be provided by a battery-charger.

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