

## TIME VARIATIONS IN ELECTROCHEMICAL PROPERTIES OF HYDROPHILIC THREE-PHASE CATALYTIC POROUS ELECTRODES

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*Dedicated to the 65th anniversary of the late Academician R. Brdička.*

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For a period of 5000 hours, the effect of the current density, electrolyte concentration, catalytic active layer thickness, and initial activity of the catalyst on the variations in electrode polarization was followed on hydrogen porous anodes, prepared from nickel and Raney nonpyrophorical nickel catalyst, and on oxygen nickel electrodes containing silver catalyst. The increase in the current density and in the KOH electrolyte concentration to 11M promoted the increase of the polarization with time. Cutting down the active layer to 0.04 cm had no appreciable influence in the case of H<sub>2</sub> anodes, in the case of O<sub>2</sub> cathodes slow changes in the degree of oxidation of the silver surface, dependent on the potential at which the electrode permanently operated, were observed. The life of a H<sub>2</sub> catalyst of a low initial activity was lower.

The service life of electrodes operating in electrochemical power sources on the principle of cumulating electric charge (secondary cells) or generating electricity through the reaction of active components fed to them (fuel cells) is of a vital importance for the economy of the source. In technical practice, the term "service life" stands for the time during which the electrode of a source is capable of delivering energy under specified conditions; depending on the mode of technical utilization (current, discharge timing, temperature, etc.), various life characteristics of one and the same source may be set. The life end point is defined by the time the power source is no longer capable of answering the purpose for which it was designed (a drop in the capacity below a stated value, a drop in the voltage to a minimum value at a constant current, etc.). These data are of a clearly technical significance and cannot serve as a measure of the changes in the electrochemical activity of the electrodes due to the existence of a number of further factors, influencing the life of the source aside from the activity of the electrodes (corrosion of the construction elements, increase in the contact resistance, impurities in the electrolyte, mechanical causes — tearing off the active layers, sealing of the gas feeding tubes, etc.).

Investigations of the service life of sources containing three-phase electrodes, carried out over the last decade, have in many instances<sup>1</sup> been made just in this way. Most data were obtained from experiments tending mainly to a technological development of electrodes, cells, and battery constructions, and to solving the problems connected with them. The principal electrochemical characteristics of porous skeletons often merged in an undefined way with the effect of a number of factors representing a possible influence on the electrode life (uniformity of the distribution

of gases, electrolyte, and reaction products over the total electrode surface<sup>2</sup>, mode of collecting and drawing the current, leakage currents in batteries with electrolyte circulation, different purity grades of the active gases, changes in the concentration and purity of the electrolyte with time, *etc.*). For this reason, the published data are difficult to compare and the results can hardly serve as a basis for drawing generalized conclusions.

Papers devoted to more rigid studies of the long-term, at least of the order of  $10^3$  hours, dependence of electrochemical properties of catalytic porous skeletons on time, are scarce<sup>3,4</sup>. Life tests not only take up the measuring sites for long periods of time but they also involve a strict circuit control of the main parameters (temperature, gas overpressure, electrolyte purity and concentration — removal of the reaction water, *etc.*). The electrotechnical and mechanical regulating elements are often of a lower service life than the cells to be tested, and their failure may bring the electrodes into such an undefined state that the incidental future changes or even break up of the electrode potential cannot be unequivocally determined. Furthermore, the equipment required to ensure a reliably operating measuring site, is so costly and place consuming that it is difficult to carry out such an amount of measurements which would permit a statistical evaluation of the many parameters involved in a life test.

It may be concluded from the results published so far that an increase in the current density and the electrolyte temperature decreases the operating life of *e.g.* hydrogen electrodes containing a Ni catalyst of the Raney type<sup>3</sup> but no reliable explanation was offered. The influence of further parameters involved in the change in the electrode catalytic skeletons activity have so far not been specified. In the present study, the influence of the electrolyte concentration, the catalytic working layer thickness, and the degree of the initial activity of the catalyst were investigated. Aside from that, the time dependence of the catalytic skeleton activity was followed at different current densities; as is well known, a change in the current density produces pronounced changes in the concentration of the electrolyte contained in the body of the skeleton pores, due to the fact that water is formed/consumed when current is drawn ( $H_2 + 2 OH^- = 2 e + 2 H_2O$ ;  $O_2 + 2 H_2O + 4 e = 4 OH^-$ ). The mechanical and corrosion resistivity of the catalyst supporting skeleton as well as the rigidity of the incorporation of the catalyst particles under the electrochemical reaction conditions may vary with time, and the utilization of the catalyst may thus be greatly influenced. In order to make the electrochemical activity of the porous catalytic skeleton the only variable, a porous system had to be employed in whose structure and mechanical properties, when followed with methods available for measuring the pore size distribution and microscope ground sections, no appreciable changes were found in the course of the life test.

## EXPERIMENTAL

Measurements were made on  $H_2$ — $O_2$  cells consisting in all cases of one two-face oxygen electrode placed between two hydrogen electrodes active only on the one side facing the oxygen electrode. The electrodes were 0.2 cm apart. The operating parts of the electrodes were two-layer discs of 2.5 cm diameter ( $S = 5 \text{ cm}^2$ ) consisting of a catalytic active layer of 0.13 cm thickness, covered with a non-active cover layer of porous nickel 0.07 cm thick. The supporting material of the skele-

ton of both layers was carbonyl nickel (USSR — GOST 9722-61, marked PNK-2). The cover layer contained 46% of pores of  $r < 1 \mu\text{m}$  and was, therefore, impermeable to gases up to  $\Delta p = 1.5 \text{ atm}$ . The active layer contained two interconnected pore systems of  $r_1 = 1$  and  $r_2 = 10$  to  $15 \mu\text{m}$  and was prepared from a mixture of powdered nickel and catalysts. Two such discs were connected by a circumferential ring made also from powdered nickel; the ring was shaped in a way to form a cavity of 0.10 cm between the layers. The electrode thus had a diameter of 3.1 cm and 0.5 cm thickness. The hydrogen electrodes had the catalytic layer on one side only, the other side was substituted with an equally thick layer of porous nickel of a pore size distribution equal to that of the cover layer. In electrodes processed for investigating the effect of the catalytic layer thickness on the life, the catalytic layer thickness from the gas side was cut down to 0.10, 0.07, and 0.04 cm, and the space difference up to 0.13 cm was filled with a non-catalytic layer of an equal porous structure, *i.e.* biporous, in order to ensure comparable mass transport conditions. The mode of spreading the powder, pressing under  $1500 \text{ kg/cm}^2$ , and sintering in  $\text{H}_2$  at  $450^\circ\text{C}$  has in detail been described previously<sup>5</sup>. The potentials of the electrodes thus obtained, measured at currents up to  $0.5 \text{ A/cm}^2$ , were reproducible within less than  $\pm 2 \text{ mV}$ . The discs carried two nickel tubes welded on opposite sides to two openings bored into the circumferential ring for feed and discharge of gases and for collecting the current.

The hydrogen electrodes were catalyzed with a dry non-pyrophorical Raney nickel prepared by leaching an alloy consisting of 50 Ni/48 Al/2 Ti in 5M-KOH at  $90^\circ\text{C}$ , washing and controlled drying<sup>6,7</sup>. When investigating the effect of the initial activity of the catalyst on the electrode life, two further catalysts of equal type were employed. One was prepared by leaching an alloy 50 Ni/50 Al, the absence of Ti being the cause of its lower activity<sup>3,8</sup>. The other catalyst with a lower activity arose by a partial deactivation of the alloy 50 Ni/48 Al/2 Ti on account of unidentified reasons, when processing a larger quantity of the catalyst in a factory equipment which most probably had not been sufficiently cleaned after the previous process. The initial activities of the catalysts were determined by measuring the differential specific polarization resistance of electrodes containing the catalysts under investigation strongly diluted with nickel powder<sup>7,8</sup>; the measurements were made at  $25^\circ\text{C}$ , when the differences in the activities became appreciable. The oxygen catalyst was represented by grains of silver which formed during the sintering process by the decomposition of silver oxalate<sup>9,10</sup> added to the active layer mixture.

#### Establishing the Long-Term Function of Electrodes

To increase the reliability of the assembly ensuring the long-term operation of the electrodes, and to make the equipment as simple as possible, the electrodes were investigated in cells containing both the oxygen and the hydrogen electrodes, in spite of the possible interplay of the electrode reaction or corrosion products soluble in the electrolyte. The electrodes were attached to a perspex glass lid sealing tightly the nickel plated cell vessel. The lid had two channels for the feed and discharge of hydrogen and oxygen; when bolted together, the lids created a gas manifold, feeding all the cells in series with both gases. The nickel feeding tubes of the electrodes, passing through the lid, served at the same time as voltage terminals connected in series. In attempting to maintain the individuality of the electrolyte of each cell, the reaction water was not removed from the circulating electrolyte, but by a more complicated system of evaporating from each cell separately by a current of dry,  $\text{CO}_2$  free air stream entering just above the electrolyte level of each cell. The lid of each of the cells contained the sensor of an electronic level indicator (essentially a nickel point); with the aid of an automatic switch, the indicator was connected to one cell after the next for a period of one hour. The assembly containing nine cells, the process was repeated once in every nine hours. The cell wall made the second pole of the a. c. control circuit. If the point was in contact with the electrolyte when switched on, a solenoid vent opened the air inlet which

remained open until the electrolyte level was lowered to cut off the contact. The quantity of the air was calculated to such a value to remove the reaction water in a period below 1 hour, during which the level control was switched on. For all the cells, the period of the air stream was registered for better control. The reaction water could thus dilute the cell electrolyte by at most 3·8% of the initial volume at a current density up to 0·1 A/cm<sup>2</sup> during one nine hour cycle. In cells operating at 0·2 A/cm<sup>2</sup>, the water was removed by a constant current of dry air evaporating approximately one half of the water formed. The other half was removed in the usual way described above. This held the maximum electrolyte concentration change under the 3·8% threshold even in this case. Electrolytes were prepared by diluting a 15N solution of a reagent grade KOH separated from the unsolved K<sub>2</sub>CO<sub>3</sub> by settling and they were exchanged every 1500 hours. Nine cells were connected in series. Their temperature was maintained at 75°C by a thermally isolated silicone oil bath. In this arrangement, no leakage currents were found between the electrodes or between the adjoining cell vessels.

Electrolytic hydrogen (99·8%, 0·2% O<sub>2</sub>) and medicinal oxygen (>99·5%) from pressure cylinders were fed to the electrodes from a central gas supply at a constant overpressure of 0·8 ± 0·02 atm. The gases were lead through flow-meters based on the principle of differential manometers which had the role of controls cutting off both the current load and the gas inlet with the aid of a non-transparent liquid and a photoelectric cell, if the gas flow exceeded or dropped below a set limit. This set-up provided for a safe operation of the whole assembly (cutting-off the gases, especially hydrogen, in case of a major leakage) and besides, prevented the possible deterioration of the electrodes by excessive load in case of a failure in the gas supply or a drop in the temperature. Prior to entering into the first cell in the series, the gas passed through a wash bottle filled with distilled water maintained at a temperature set by trial and error to such a value which prevented the gas from carrying away water vapour from the first cell. In this way the conditions (temperature and concentration of the electrolyte) were identical in all the cells. The oxygen and hydrogen passed through the nine cells countercurrent-wise, *i.e.* the first cell for oxygen to enter was the last cell for hydrogen to pass through. An excess of either gas, amounting to 10% of the entering quantity of oxygen and 5% of the quantity of hydrogen, provided for the removal of inert components trapped in the electrodes after consumption of the reactant gases.

### Electrical Measurements

Each assembly of nine cells was discharged in a constant regime *via* an adjustable resistor. Each three adjoining cells in the series were equal in their operating regime, and the results quoted are a mean of the three values obtained. The electrodes were of a highly reproducible character and the deviations measured did not exceed ±2 mV in the case of H<sub>2</sub> and ±5 mV in the case of O<sub>2</sub> electrodes even after long time periods. The electrode potentials were measured against a Hg/HgO electrode in 7M-KOH with the aid of a compensation bridge QTK (Metra, Blansko). The reference electrode was connected to the cell with a salt bridge, containing also 7M-KOH, whose orifice was passed through a hole in the lid and located immediately above the electrode. The cell voltages were measured with the same compensation bridge. Repeated measurements during which the salt bridge was taken in and out proved that differences in the potential values obtained on one and the same electrode did not exceed several mV, so that the procedure was sufficiently accurate for following the time changes in the electrode polarization. To gain insight into the operation of the cells during the time the assembly was unattended, some of the cell potentials were continuously registered.

The unpyrophorical nickel catalyst was, after incorporation into the electrode skeleton, in an inactive form, and had to be activated. This was done after placing the cells on the measuring sites

and filling with 7N-KOH ( $70 \text{ cm}^3/\text{cell}$ ). The temperature was raised to  $75^\circ\text{C}$  and the electrodes were flushed with  $100 \text{ cm}^3 \text{ H}_2/\text{h}$  at  $\Delta p = 0.8 \text{ atm}$  for 72 hours. The electrodes reached the value of the reversible  $\text{H}_2$  potential after several tens of minutes already, but the activation was prolonged to the extreme on account of the fact that the initial activity of the catalyst proved to be of importance for the electrode life. During activation of the hydrogen electrodes, the oxygen electrodes were filled with stationary  $\text{H}_2$  at the same overpressure and their potential was  $-920 \text{ mV [Hg/HgO]}$ . The uniformity of the activity of all electrodes was controlled by measuring their potential at  $75^\circ\text{C}$  in 7N-KOH at  $i = 0.1 \text{ A/cm}^2$  and only then the conditions were adjusted for investigating the effect of the electrolyte concentration and current density.

## RESULTS AND DISCUSSION

As expected, a higher current density produced a higher rate in the polarization increase of the hydrogen anodes (Fig. 1). The dispersion variance of the experimental points is due to two reasons. 1. In spite of all the precautions taken to ensure a fail-safe continuous discharge, a few failures — mostly of the regulating system — brought about an automatic cut-off of the discharge circuits. The  $\text{H}_2$  anodes thus returned to the reversible hydrogen potential for various periods of time until the defect was discovered. It has already been reported<sup>11</sup> that these anodes may be recovered even after a potential break-up caused by oxidation of the catalyst surface. The recovering process is analogous to the above quoted activation of till that time unused electrodes, *i.e.* the catalytic skeleton is left in contact with a hydrogen atmosphere and with electrolyte maintained at an elevated temperature. In the case of the load cut-off during the defect mentioned above, such a recovery must certainly have taken place

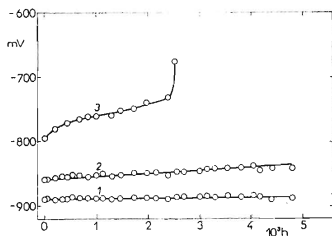


FIG. 1

Time-Potential Variations of  $\text{H}_2$  Anodes at Different Current Densities

7M-KOH,  $t = 75^\circ\text{C}$ ,  $\Delta p_{\text{H}_2} = 0.8 \text{ atm}$ , continuous discharge; 1  $i = 0.05 \text{ A/cm}^2$ ; 2  $i = 0.10 \text{ A/cm}^2$ ; 3  $i = 0.20 \text{ A/cm}^2$ .

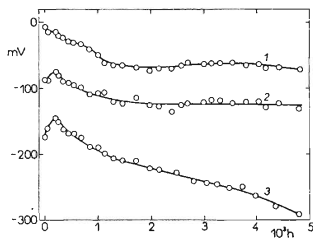


FIG. 2

Time-Potential Variations of  $\text{O}_2$  Cathodes at Various Current Densities

7M-KOH,  $t = 75^\circ\text{C}$ ,  $\Delta p_{\text{O}_2} = 0.8 \text{ atm}$ , continuous discharge; 1  $i = 0.05 \text{ A/cm}^2$ ; 2  $i = 0.10 \text{ A/cm}^2$ ; 3  $i = 0.20 \text{ A/cm}^2$ .

in at least some active centers of the Ni catalyst which had partly been oxidized during the long-term operation. A temporary drop in the anode polarization was a direct consequence of this process. 2. The other cause of the dispersion variance of the experimental points on the curves of both the H<sub>2</sub> and O<sub>2</sub> electrodes was due to the discontinuity of the removal of the reaction water from the electrolyte. All the cells under investigation were measured at the same time. One of the three cell assembly, yielding the values for the mean value calculation, could, at the time of the measurement, be just before or after the evaporation of the water by the dry air current; if a cell was just under evaporation, it was measured only after the temperature which during evaporation dropped by as much as 5°, was recovered. Even though the extreme concentration values did not exceed 3.8%, the polarization variations due to this effect were appreciable especially in the case of O<sub>2</sub> cathodes, whose initial polarization is high on account of the irreversibility of the current generating reaction; in the case of H<sub>2</sub> anodes the effect was noticeable at higher polarizations and toward the electrode life end point.

The course of the increase of the polarization of the H<sub>2</sub> anodes was linear at 0.05 to 0.10 A/cm<sup>2</sup> current densities. When the electrode was loaded with 0.20 A/cm<sup>2</sup>, the rate of the polarization increase was initially higher and only after a certain period became linear again. This initial larger deterioration of the catalytic properties of the anodes was observed in all cases in which the potential was shifted from -920 mV into the regions of -800 mV, irrespective of whether the shift was caused by the initial lower catalytic activity (see Fig. 6, curve 2, 3), or by the increased current density, or by a drop in the temperature. The oxides of nickel are not capable of catalyzing the anodic oxidation of hydrogen. For corrosion reasons a nickel catalyst cannot perform under the given conditions at potentials more positive than -760 mV<sup>14</sup>. It may also be possible that when approaching this region, the catalyst behaves differently than it does when in the more negative potential regions, on account of the formation of non-stoichiometric passivating films. A comparison may be

TABLE I

Rate of Decrease of the Activity of the Catalytic Skeleton of Hydrogen Anodes as an Exponential Function of the Current Density

$t = 75^{\circ}\text{C}$ , 7M-KOH,  $\Delta p_{\text{H}_2} = 0.8$  atm.

$\Delta E$ , mV/10 <sup>3</sup> h	$i$ , A/cm <sup>2</sup>	$\Delta E/i^2$
1.0	0.05	$4.0 \cdot 10^2$
4.7	0.10	$4.7 \cdot 10^2$
18.3	0.20	$4.6 \cdot 10^2$

TABLE II

Variations of Polarization of Hydrogen and Oxygen Electrodes with Time in Electrolytes of Various Concentrations

$$\Delta E[\text{mV}/10^3 \text{ h}], 75^\circ\text{C}, i = \text{const.} = 0.10 \text{ A}/\text{cm}^2, \Delta p_{\text{H}_2} = 0.8 \text{ atm.}, \Delta p_{\text{O}_2} = 0.8 \text{ atm.}$$

El.	3M	7M	11M
H <sub>2</sub>	+ 4	+ 5	+ 13
O <sub>2</sub>	- 13	- 12	- 65

suggested with the very slow changes (of the order of  $10^3$  hours) of the silver catalyst surface, connected with the shift of its working potential, as will be discussed below. The initial stabilization of the nickel catalyst surface, taking place in the course of about 500 hours, is followed by a linear increase of the polarization with time at a rate of  $18.3 \text{ mV}/10^3 \text{ h}$ , *i.e.* a much higher rate than that encountered at lower current densities ( $i = 0.05 \text{ A}/\text{cm}^2$ ,  $k = 1 \text{ mV}/10^3 \text{ h}$ ;  $i = 0.10 \text{ A}/\text{cm}^2$ ,  $k = 4.7 \text{ mV}/10^3 \text{ h}$ ). After 2500 hours a rapid raise of the anode polarization set in which was a sign of a complete oxidation of the catalyst surface. The same effect is suggested by the shape of the curves 1 and 2 in Fig. 1, concerning lower current densities; the slopes of the curves being smaller, the electrode life end point is more remote. In electrodes of a less perfect construction, manufactured previously, defined by a less uniform distribution of hydrogen in the catalytic skeleton, the life end point of the same catalyst was reached after 17000 hours at  $95^\circ\text{C}$  and  $0.1 \text{ A}/\text{cm}^2$ . Table I, depicting the slopes ( $\Delta E[\text{mV}/10^3 \text{ h}]$ ) of curves 1 and 2 and the slope of the linear portion of curve 3 from Fig. 1 as a measure of the service life, shows that the dependence of the operating life of the catalytic skeleton with a nickel catalyst on the current density at a constant temperature and electrolyte concentration was, in a rough approximation, exponential. In some cases it was observed that even when oxidized the Ni catalyst yielded currents of considerably high densities ( $i = 0.2 \text{ A}/\text{cm}^2$ ) but at a more positive and poorly defined potential which varied with time in the range  $-400$  to  $-200 \text{ mV}$ ; the dependence of such a cell on the temperature was exceptionally high (as high as  $25 \text{ mV}/^\circ\text{C}$ ) as compared to that of a catalytic H<sub>2</sub> anode (about  $6 \text{ mV}/^\circ\text{C}$ ). This points to a principally different mechanism of the current generating reaction. The most probable explanation is that the nickel oxides were reduced by gaseous hydrogen (compare with the possibility of recovering the electrodes<sup>11</sup>) with a subsequent electrochemical oxidation of the reduced nickel, or that an electrochemical oxidation of hydrogen was proceeding with a correspondingly higher overvoltage on an oxidized nickel surface.

The changes in the potential of the oxygen cathodes with time at various current densities will be found in Fig. 2. At  $i = 0.05 \text{ A}/\text{cm}^2$  (curve 1) and  $0.10 \text{ A}/\text{cm}^2$  (curve 2),

the initial stabilization of the porous skeleton surface, accompanied by a larger increase of polarization, was followed by slow changes of the potential. At  $i = 0.20 \text{ A/cm}^2$ , the polarization increase was visibly more rapid than at lower current densities, the rate of its increase remaining on the same level during the total period followed. As will be discussed later, the catalytic activity of the silver catalyst would be relatively higher at increasing current densities, as they involve a shift of the working potential of the electrode into more favourable more negative regions. This concept is also supported by the inception of the curves 2 and 3 for regions up to 200 hours. At  $i = 0.20 \text{ A/cm}^2$ , however, it seems to be rather the electrolyte concentration which is the limiting factor of the catalytic skeleton life. On account of the consumption of water by the electrochemical reaction, which is proportional to the current density, the concentration of the electrolyte contained in the pores of the skeleton becomes higher than that in the bulk electrolyte of the cell. It may be seen in Table II that the increase of polarization with time (loss of activity) of the silver catalyst was more rapid if the concentration of the bulk electrolyte in the cell was raised from 7 to 11N. There is no explanation for this phenomenon so far, but the slow rate of the changes seems to point to a connection with the changes in the structure of the catalyst surface when it operates in a highly concentrated electrolyte. It may be drawn from the results obtained on these electrodes that if utilized for constructing a high-life fuel battery, a constant load should not exceed  $0.1 \text{ A/cm}^2$ . Higher current drains may only be applied for short periods.

The effect of the concentration of the bulk electrolyte on the time course of the terminal voltage in a  $\text{H}_2\text{--O}_2$  cell constructed with the above type electrodes at  $i = \text{const.} = 0.1 \text{ A/cm}^2$  is depicted in Fig. 3. Curves 1 and 2 for 3M and 7M-KOH, respectively, demonstrate that there was no pronounced influence of this range of concentration changes on the long-term behaviour of the electrodes. An essential change was produced by 11M-KOH (curve 3). The initial potential value is already

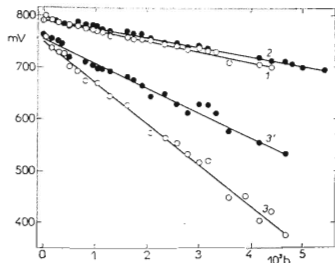


FIG. 3

Variations in Terminal Voltage of  $\text{H}_2\text{--O}_2$  Cells with Time at Various Electrolyte Concentrations

$t = 75^\circ\text{C}$ ,  $\Delta p$  of gases 0.8 atm, continuous discharge  $0.1 \text{ A/cm}^2$ ; 1 3M-KOH; 2 7M-KOH; 3 and 3' 11M-KOH.



lower and its drop with time is four times as fast as it is in the case of 3M and 7M-KOH. This degradation is due to the influence of the concentrated electrolyte on the inner surface of the porous catalytic skeleton, especially in the case of oxygen electrodes. Curve 3' with a slower drop of the terminal voltage pertains to a cell containing an electrolyte of the same concentration as in the cell 3, whose oxygen electrodes were fed with oxygen which, as the feeding occurs in series, was pre-saturated with water vapour over 7M-KOH in the preceding triad of the cells. The amount of water, corresponding to the difference between the saturated vapour pressure over 7M-KOH and 11M-KOH, diluted the 11M-KOH in the proximity of the reaction zone, influencing thus favourably the function of the silver catalyst.

It was not possible to separate with accuracy the contributions of the individual electrodes to the terminal voltage values, in view of the difficulties involved in converting the potential values obtained by measurements with a Hg/HgO electrode with 7M-KOH to comparable values. These difficulties (exact determination of liquid junction potentials) would not be eliminated when employing reference electrodes containing electrolytes of the same concentration as in the cells tested. Not even then would a comparison between various concentrations be possible. The behaviour of individual electrodes was, therefore, compared only on the basis of their relative potential variations with time, these values being for the period of the test close to constant. It will be seen from Table II that there were no large differences between the changes pertaining to 7M and 3M concentrations for either H<sub>2</sub> or O<sub>2</sub> electrodes.

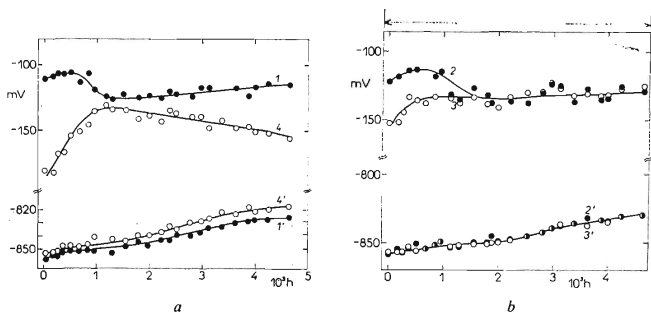


FIG. 4

Time-Potential Variations of O<sub>2</sub> Cathodes and H<sub>2</sub> Anodes at Various Catalytic Active Layer Thickness  $l$

7M-KOH,  $t = 75^\circ\text{C}$ ,  $\Delta p = 0.8$  atm, continuous discharge  $0.1$  A/cm<sup>2</sup>; *a* 1 O<sub>2</sub>,  $l = 0.13$  cm; 1' H<sub>2</sub>,  $l = 0.13$  cm; 4 O<sub>2</sub>,  $l = 0.04$  cm; 4' H<sub>2</sub>,  $l = 0.04$  cm. *b* 2 O<sub>2</sub>,  $l = 0.10$  cm; 2' H<sub>2</sub>,  $l = 0.10$  cm; 3 O<sub>2</sub>,  $l = 0.07$  cm; 3' H<sub>2</sub>,  $l = 0.07$  cm.

In this concentration region, the rate of the polarization increase is low, being approximately by threefold higher for oxygen electrodes. This difference is probably due to the different degree of reversibility of the reactions proceeding at either electrodes, because equal variations in the experimental conditions (for instance a drop in the temperature, increase of the current load *etc.*) produced in all cases a larger polarization increase in the case of the oxygen cathode than the hydrogen anode; here the oxidation of hydrogen takes place at potentials closer to the theoretical reversible potential of a hydrogen electrode in the same medium than does the reduction of oxygen at the other electrode. Utilizing 11M-KOH produced a pronounced change in either case. In the case of the oxygen electrode, the rate of the loss of the activity increased in comparison with lower concentrations about five-fold, in the case of the hydrogen electrode only about three-fold. The negative influence of the electrolyte concentration on the silver skeleton activity was observed in all cases, irrespective of whether the concentration in the close proximity of the catalyst particles was raised as a consequence of the bulk electrolyte concentration increase, a current density increase (see above), or a decrease in the catalytic active layer thickness at constant current, as will be explained below.

In a hydrogen catalytic skeleton, an increase in the KOH concentration from 7M to 11M produced an increase in polarization at the very beginning of the test ( $\Delta E = 64$  mV or 91.6 mV at  $i = 0.10$  A/cm<sup>2</sup>). Repeated tests then confirmed that

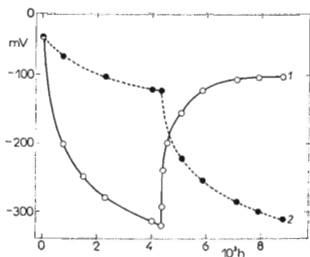


FIG. 5

Changes of the Catalytic Layer Activity of O<sub>2</sub> Cathodes with Time in Dependence on the Long-Term Polarization Value

7M-KOH,  $t = 95^\circ\text{C}$ ,  $\Delta p_{\text{O}_2} = 0.8$  atm, continuous discharge; 1  $i = 10^{-3}$  A/cm<sup>2</sup>; 2  $i = 10^{-1}$  A/cm<sup>2</sup>.

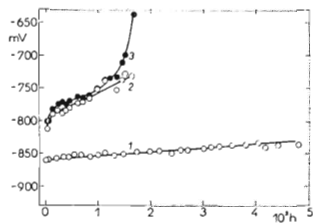


FIG. 6

Effect of Initial Activity of Ni Catalyst on the Life of Porous H<sub>2</sub> Anodes

7M-KOH,  $t = 75^\circ\text{C}$ ,  $\Delta p_{\text{H}_2} = 0.8$  atm, continuous discharge 0.1 A/cm<sup>2</sup>; for catalysts specification see Table II. The curve numbers are identical with those contained in the Table.

a higher increase of the polarization with time, *i.e.* a shorter life was indicated by a higher initial polarization of a nickel hydrogen anode (compare Figs 1 and 6). The polarization increase in 11M-KOH may be due to an interplay of several factors (decreased conductivity of the electrolyte, inhibited diffusion, lower solubility of hydrogen, *etc.*). The increase in the polarization indicates that the catalyst operates under more difficult conditions and, therefore, closer to the potential of the starting oxidation of nickel, with all the consequences mentioned above.

A difference in the thickness of the active layer of H<sub>2</sub> anodes led to only small differences of several mV in the initial polarization, as is seen in Figs 4a and 4b. In harmony with what was stated above, the course of the potential-time dependence of electrodes with a different active layer thickness was not markedly influenced. This indicated that in all electrodes the current was generated in a layer of 0.04 cm thickness or below; this observation is in harmony with the theoretical study by Micka<sup>12</sup>. In the case of oxygen cathodes, the initial polarization was the lower the larger the active surface available, *i.e.* the larger the catalytic layer thickness. In the course of the first 1500 hours the electrodes with higher initial polarization were gradually activated, whereas the activity of electrodes with a lower initial polarization somewhat decreased; at the end of this period the electrodes were virtually equal. The further change of polarization was only slow with the exception of the electrode with the least catalytic layer thickness whose activity slowly decreased. If at a constant current load, a higher local electrolyte concentration is assumed in the proximity of the silver catalyst particles in the thin layer than there is in the thicker layers (on account of a higher absolute current load per unit of the operating catalytic surface proper), the decrease in the activity is then analogous to the above discussed negative influence of the electrolyte concentration increase on the time course of the polarization of the oxygen cathodes containing silver catalyst.

As is well known, oxides on a silver surface inhibit the electrochemical reduction of oxygen<sup>13</sup>. Such oxide films may certainly be expected to form on the surface of the Ag catalyst of oxygen electrodes both immediately after their preparation (when

TABLE III  
Initial Values of Differential Specific Polarization Resistance  $R_s$  of Nickel Catalysts

No	Catalyst prepared from alloy	$R_s$ $\Omega \cdot \text{cm}^2$
1	50 Ni/48 Al/2 Ti	1.22
2	50 Ni/48 Al/2 Ti deactivated	2.63
3	50 Ni/50 Al	8.34

taken out from the  $H_2$  atmosphere and exposed to air) and if their body is filled with oxygen, when wetted with electrolyte at an elevated temperature. The momentary state of such a film, partly passivating the surface, proved to be, in an operating oxygen cathode, the result of a very slow establishment of an equilibrium (of the order of  $10^3$  hours) between the chemical oxidating influence of the gaseous oxygen on the silver surface and between the electrochemical reducing influence of the potentials more negative than those of the stoichiometric silver oxides. This may be drawn from Fig. 5 showing the time dependence of the variations of the catalytic activity of the  $O_2$  active layer on the potential at which the electrode was held for a long period of time. The measure of the activity was in this case the potential which was established at an electrode loaded with  $0.10 \text{ A/cm}^2$ . The group of electrodes which is characterized by curve 1 was permanently loaded with  $10^{-3} \text{ A/cm}^2$  and maintained, therefore, at a very positive potential value of approximately  $+100 \text{ mV}$ . The long-term influence of this potential value resulted in a slow steady decrease of the activity of the catalytic skeleton (measured always after 1 h load at  $0.1 \text{ A/cm}^2$ ). After 4360 hours the load of the electrodes was raised to  $0.10 \text{ A/cm}^2$  shifting the potential permanently into far more negative regions. From this time on, the activity started to increase but only after 2–3 thousand hours it acquired a constant value.

Electrodes characterized by curve 2 were on the contrary initially loaded with a steady current of  $0.10 \text{ A/cm}^2$ ; their activity decreased approximately in the same way as was usual for this type of skeleton. After 4360 hours the load was changed to  $10^{-3} \text{ A/cm}^2$  (*i.e.* to the more positive potential region of  $+120 \text{ mV}$ ); the decrease of the activity with time which set in at this moment was similar to that corresponding to the appropriate portion of curve 1. It may, therefore, be concluded from Fig. 5 that the activity of the silver catalytic skeleton was at any moment the result of a very slow establishment of an equilibrium which could be influenced by the potential at which the skeleton was permanently maintained. It will be seen from Figs 4a and 4b that similar processes of slow equilibria were establishing in the first period of the investigation of the life of electrodes with various catalytic layer thicknesses or with various current loads (Fig. 2).

The course of the time dependence of the  $H_2$  anode potentials with Ni catalysts of a different initial activity (see Table III) is shown in Fig. 6. The life of the catalytic skeleton prepared from a less active catalyst is lower, which may be due to the shift of the incipient polarization into more positive regions, discussed above. A comparison of the results contained in Fig. 6 and Table III reveals that the low  $R_p$  value cannot in itself be taken as an indicator of a high life of the catalyst. Whereas the values 1 and 2 in Table III are very close, an almost identical life was exhibited by catalysts 2 and 3. As already mentioned in the experimental part of this paper, catalyst 2 prepared from the same alloy as catalyst 1 was deactivated in the preparation process. This is an evidence that the life of the electrochemical Raney nickel catalyst may be influenced not only by the structure of the surface as determined

by the quality of the initial alloy, but also and to a great extent by the conditions of its processing.

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