

CONTRIBUTIONS TO THE MECHANISM OF RANEY NICKEL DSK ELECTRODES

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1. Introduction

A decade ago Justi et al. (1) have disclosed the DSK (double skeleton katalyst) system of gas diffusion electrodes consisting of a supporting homeoporous macroskeleton with embedded homogenized grains of catalytically active microskeletons of Raney metal type. A primary goal of this system has been to avoid platinum metal catalysts and to improve hitherto less powerful electrocatalysts such as Raney nickel. This is the main reason why the DSK system does not meet the requirements of space technology but continues being of actual importance for terrestrial applications such as electrotraction. Apart from its abundance nickel has the peculiar advantage to store great amounts of hydrogen and to facilitate in this way the operation of hydrogen nickel anodes even under overload and as accumulator electrode. In fact, our own group (2) and Russian (3) and Czechoslovakian (4) laboratories have made remarkable progress already in the preparation of new Raney nickel catalysts which are not pyrophoric despite of increased activity. For optimum construction and operation of DSK electrodes with nickel macroskeleton and microskeleton a detailed knowledge of reversible and irreversible oxidation and corrosion processes seems to be necessary.

From the work of formation of nickelhydroxide $\text{Ni}(\text{OH})_2$ -105.6 kcal/mole and of water -56.69 kcal/mole the enthalpy of formation of the reaction $\text{Ni}(\text{OH})_2 + \text{H}_2 \longrightarrow \text{Ni} + \text{H}_2\text{O}$ may be calculated as -7.78 kcal/mole. Hence the potential of the reversible $\text{Ni}(\text{OH})_2$ electrode vs H_2 electrode in the same electrolyte is +168 mv. This means that Ni in this anode will be oxidized already at a polarization of 170 mv. Moreover it is known that nickel in alkaline electrolyte is coated by a passivating layer. Therefore, the question was how these layers will influence the porosity of the DSK anodes and the catalytic activity of the Raney Ni. In Raney Ni with its large inner surface about one out of four atoms belongs to the surface and, therefore, if only the surface atoms will be oxidized this would mean a considerable increase of volume and decrease of porosity, a change of surface structure and perhaps of the electronic structure of the catalyst grains. Such changes should be investigated by measurements of porosity, of weight, catalytic activity including gas consumption and of electric resistance vs state of oxidation. Such measurements are described below and their teachings for construction and operation of DSK anodes are discussed.

2. Influence of oxidation on porosity of DSK nickel anodes

If one places an electrode disk A as separating diaphragm between two electrolyte spaces the liquid may flow through the electrode and the pressure drop Δp at said electrode may be measured. As shown by fig. 1 two additional electrodes B are placed on each side permitting to send a direct current I through the middle electrode and to measure the potential drop $\Delta \phi$ at two more reference electrodes C in the vicinity of electrode A. In this configuration the Ni DSK electrode was gradually oxidized anodically departing from the hydrogen

potential and in this way both the flow resistance and electric diaphragm resistance are measured as function of the state of oxidation of the electrode A (5). Fig. 2 shows both resistances vs electrode potential against hydrogen in the same electrolyte. Both resistances are increased suddenly at about +150 mv what may be explained as filling up the pores by nickel hydroxide layers at its potential of formation. Corresponding experiments with carbonylnickel electrodes without Raney nickel failed to show such resistance changes and therefore, it is concluded that the Raney nickel alone is responsible for the darning of electrode pores.

3. Inactivation of catalyst by $\text{Ni}(\text{OH})_2$ coating layers

3.1 Overloading a Raney Ni DSK anode

Together with the formation of the $\text{Ni}(\text{OH})_2$ coating layer the catalytic activity of Raney nickel is lost as shown by experiment 1 in fig. 3. In this diagram is shown the potentiostatically controlled electric current I and the hydrogen flow \dot{Q} consumed by the anode and expressed by its ampere equivalent vs time in minutes. In this experiment the electrode was discharged with a polarization of +930 mv. In the beginning there is a rather high current of 6 amp corresponding to 240 ma/cm² at 20°C which is fed nearly completely by the hydrogen consumption of the electrode. But the hydrogen influx remains always somewhat smaller than the electric current and the difference is supplied from the electrochemical capacity causing a gradual oxidation of the catalyst. From the decrease of electric current and the hydrogen resorption per unit time one may see the gradual deterioration of the anode.

3.2 The process of recovery of the DSK Raney Ni anode

If one waits until there flows but a little portion of the initial electric current and if one interrupts thereupon the current the hydrogen consumption will first decrease considerably, then remain constant some time and will pass afterwards a steep maximum, cf. fig. 4.

In this diagram is also shown the electric potential ϕ as function of time during this recovery period. At the left hand nadir of the maximum this is at the beginning of the strong hydrogen consumption the potential has reached the value of +170 mv against reversible hydrogen potential. Therefore, it is plausible to explain this peak as consequence of an autocatalytic reduction of the $\text{Ni}(\text{OH})_2$ layer by gaseous molecular hydrogen. At some single germs of the surface there is activated the hydrogen and dissolved anodically. The $\text{Ni}(\text{OH})_2$ layer is reduced cathodically at the same velocity next to the germs caused by local element effect. The autocatalysis consists in the ability of the nickel atoms formed by the reduction to accelerate subsequent hydrogen resorption from the gas phase. Therefore, at the beginning of the expansion of the above mentioned active areas the hydrogen supply will be accelerated until the nickel hydroxide areas are diminished considerably. There will remain a small residual hydrogen influx caused by diffusion of hydrogen into remote regions far off the surface (6). If one extends this recovery process over several days the electrode may reach the same performance as before. But under certain circumstances one observes a deterioration of the electrochemical performance which may be understood as the formation of another "aged" phase of nickelhydroxide, as in the corresponding case of Cd (7).

4. Ageing of nickel hydroxide layers

4.1 Recovery processes after potentiostatic anodic oxidation

During the experiments described above the state of the catalyst inside the electrode was not homogenous for it was under gas pressure during overloading and was divided in an area accessible to oxidation and an unaccessible one. To reach well defined conditions we have flooded the whole electrode with electrolyte and subsequently discharged potentiostatically at a potential of +350 mv against hydrogen during 15 hours. Then the electrode was pressurized again with hydrogen and both hydrogen consumption and potential was measured during 9 hours, cf. fig. 5. The experiment was repeated on 4 following days. From the curves 2, 3, 4 and 5 it may be seen that the maxima of subsequent experiments are setting in respectively later and are decreasing each time. Integration of the \dot{Q} curves shows that charge Q received decreases from one experiment to the following one. If one compares the hydrogen amount consumed during one experiment with the oxidation charge withdrawn previously one will state that it amounts to about 70 % only. This means that during each experiment a part of the $\text{Ni}(\text{OH})_2$ is not reduced. Whereas most of the $\text{Ni}(\text{OH})_2$ is reduced spontaneously as soon as the nickel hydroxide potential is reached, the remainder is transformed in a less reducible phase the reduction of which needs several days. This is what we call "aged" nickel hydroxide.

4.2 Electronic conductivity of Raney Ni as function of state of oxidation

All details of the reaction process at Raney Ni catalysts should be disclosed if one investigates various physical properties during oxidation and subsequent reduction. In connection with the electronic state of catalyst it will be important to measure the electronic conductivity. Therefore, we have pressed under water Raney nickel powder with a pressure of 1 to/cm² at room temperature and cut from the sheet thus produced a specimen of 37.3 x 6.1 x 3.3 mm. This rod St was provided with two current and potential wires (I and P) and suspended in 6n KOH solution on one beam of a balance, as shown by fig. 6. The experiment was performed in this way: starting from the hydrogen potential we have drained anodic charges in subsequent little portions and have measured simultaneously the electric resistance, weight and potential of the specimen after having reached a steady state. Fig. 7 shows the results. From the shape of the potential curve φ vs charge L one takes cognizance of the beginning hydroxide formation after 11 amp. min discharge. Before hydroxide formation only hydrogen was withdrawn at negative potentials, the region 1 in fig. 7. During this period the resistance R of the Raney Ni specimen drops from about 7.4 to 5.3 mohms, and simultaneously the weight decreases proportional to the charge L withdrawn. This part of the phenomena observed is understandable as caused by the removal of hydrogen built in the nickel lattice during activation, and the reduction of weight is caused in this way. The process is supported by additional removal of aluminum. Now one may expect that according to the well known experiments of Suhrmann (8) the removal of hydrogen as donor is connected with a resistance increase. Surprisingly that is not the case but we observe a considerable decrease of resistance understandable as removal of scattering centres.

During the formation of nickel hydroxide both electric resistance and weight is increasing nearly proportional to the charge, see region 2 in fig. 7. The increase of resistance is explained by the depletion of conductivity electrons which are consumed by the oxidation process. The weight increase is due to the augmentation of the specimen. But the increase of volume must also be considered because the increase of buoyancy causes a apparent decrease in weight. The change of weight observed is the difference of the real change Δg minus the change of buoyancy $\Delta V \cdot \rho$. For the reaction $\text{Ni} + \text{Ni}(\text{OH})_2$ is $\Delta g = 17 \text{ g/val}$, $V = 8.01 \text{ cm}^3/\text{val}$ and $\rho = 1.257 \text{ g/cm}^3$. The expected weight change $\Delta g = 17 - 10 = 7 \text{ g/val}$ is in good agreement with the measured value of 6.85.

Until complete oxidation the resistance increases by nearly 300 %, but continues behaving metallic as proved by its always positive coefficient of temperature. If one tries to reduce the specimen electrochemically one reaches very soon the hydrogen potential without an appreciable reduction of the catalyst. Accordingly the resistance remains relatively high, about 200 % above the lowest resistance value. Also evolution of hydrogen at higher polarization changes the resistance hardly. Even here appears a hysteresis showing that nickel hydroxide reduction may be a slow process.

4.3 Interpretation of ageing

Certainly the reduction of nickel hydroxide may be accelerated by raising the temperature. To measure this effect we have reduced cathodically the specimen at different temperatures at a potential of + 80 mv against reversible hydrogen or else - 88 mv against nickel hydroxide potential t . At this potential we have measured the currents I dependent on temperature. Fig. 8 shows $\log I$ vs $1/T$. The linear character proves that the speed controlling process is a purely chemical reaction with an activation energy of 15.9 kcal/mole and occurs prior to the electrochemical process. If one assumes that the cathodic reduction of $\text{Ni}(\text{OH})_2$ proceeds according to $\text{Ni}(\text{OH})_2 + e^- \rightarrow \text{NiOH} + \text{OH}^-$, the speed limiting chemical process should be the transformation of aged $\text{Ni}(\text{OH})_2$ into a phase appropriate for the electrochemical discharge process. One plausible explanation is that during the ageing nickelhydroxide forms NiO by splitting off water (9), which must reformed in hydroxide again by absorption of water. The maximum work of the water splitting reaction is $\Delta G = G_{\text{NiO}} + G_{\text{H}_2\text{O}} - G_{\text{Ni}(\text{OH})_2} = 2.79 \text{ kcal/mole}$ and hence rather little, but according to the above mentioned high energy of activation there is a high energy peak in the course of reaction, as shown by fig. 9. Another explanation of the strong temperature dependence but little potential dependence of the cathodic reduction of Raney Ni is a polymorphism of nickel hydroxide as discussed by Bode (10). Similar observations on $\text{Cd}(\text{OH})_2$ of Gottlieb (7) have been mentioned already.

5. Discussion of results and outlook

The experiments described have given the teaching for the operation of anodes with nickel catalyst that one should avoid the formation of nickelhydroxide layers. Nevertheless this does not mean one must not operate such hydrogen anodes at polarizations exceeding 170 mv, for the ohmic I.R drop and concentra-

tion polarization are not included and, moreover, hydroxide formation will insert at more positive potentials in dilute KOH solution. In fact, the electrode will supply at polarizations of about 150 mv such great current densities that the electrolyte inside the pores will be diluted and the current will be limited by lack of OH⁻ ions. Therefore, under normal conditions the current is not limited by hydroxide formation but by concentration polarization and we have developed a method to increase the limiting current density and to decrease the polarization by continuous or intermittent rinsing with small amounts of concentrated KOH(11).

In conclusion it should be mentioned that the stationary polarization current performance of a Raney nickel anode may be improved considerably by a transient positivation of electrode potential. As example fig. 10 presents two curves of the same electrode, which was oxidized anodically one hour at 350 mv against hydrogen and then dried in air. After reduction with molecular hydrogen the electrode showed an improved performance with a polarization resistance of 1.2 ohm. cm².

Although the present investigations into the mechanism of Raney catalyst electrodes have contributed interesting informations about construction and operation of electrodes avoiding rare metal catalysts the authors feel we are only at the beginning of a fully utilizing the possibilities of such electrodes both in fuel cells and accumulators.

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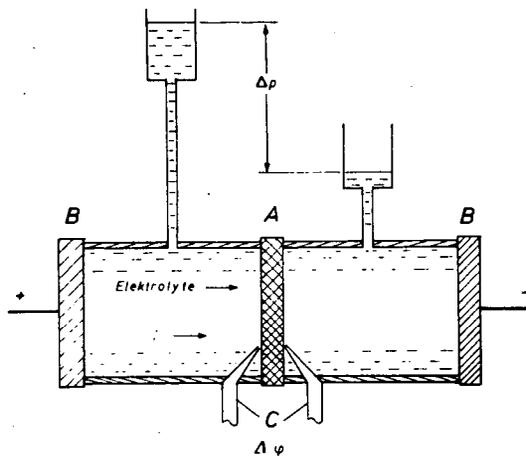


Fig. 1. Schematic arrangement for the simultaneous measurement of liquid flow resistance and electric diaphragm resistance of a porous electrode A. B outer electrodes, C Luggin capillaries.

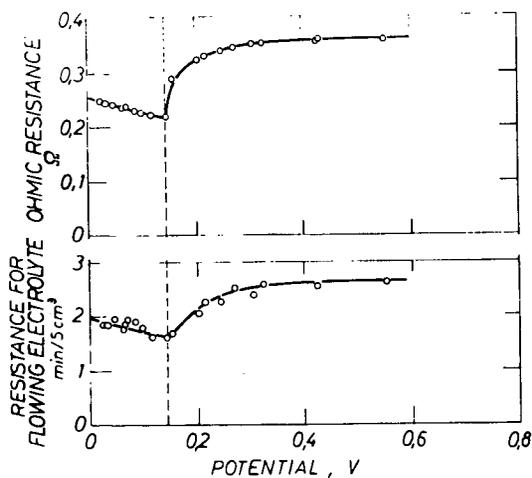


Fig. 2. Diaphragm resistance (upper curve) and liquid flow resistance (lower curve) of a Raney nickel DSK anode vs electrode potential against hydrogen reference electrode in the same 6 n KOH.

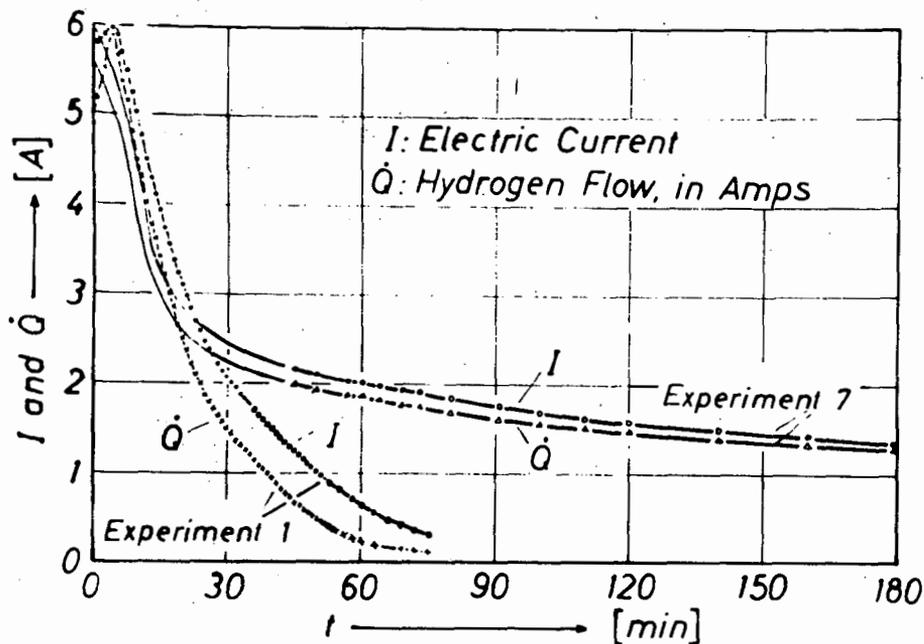


Fig. 3. Potentiostatic discharging of a Raney nickel DSK anode at a polarization of +942 mv. Experiments no. 1 and 7. Current I surpassing the equivalent hydrogen influx \dot{Q} is plotted vs. time in min.

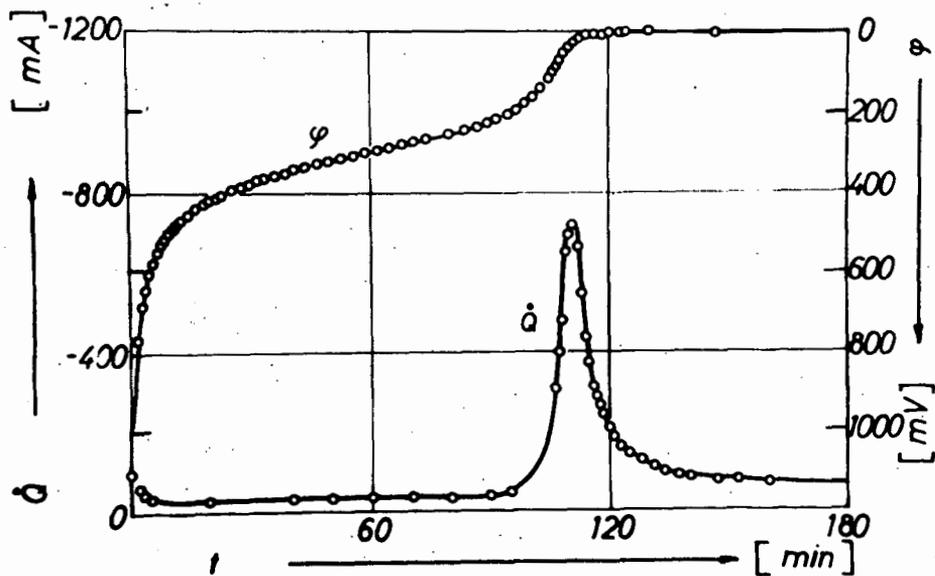


Fig. 4. Electrode potential ϕ against hydrogen reference electrode in the same electrolyte and influx \dot{Q} of hydrogen vs. time after switching off the potentiostatic loading of experiment 1 in fig. 3.

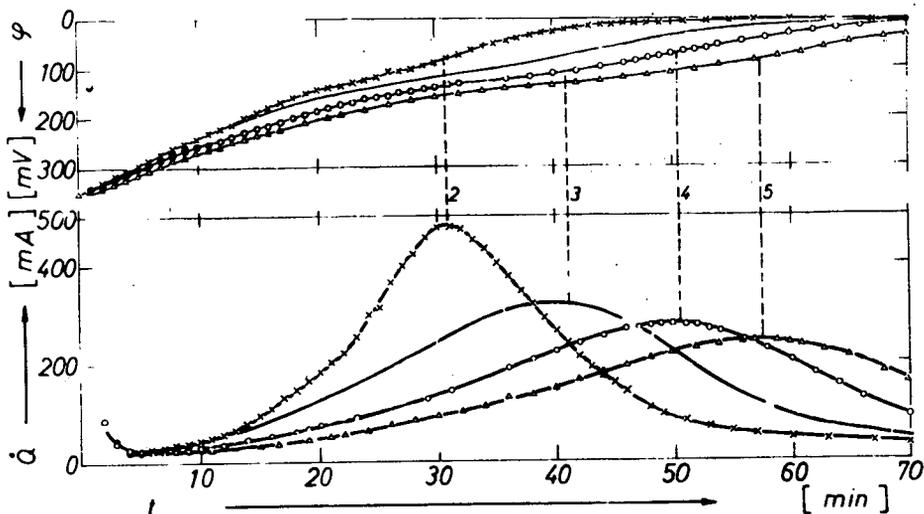


Fig. 5. Four recovering processes, showing the aging of $\text{Ni}(\text{OH})_2$. (Meaning of the symbols cf. fig. 4). Before each experiment the hydrogen electrode was potentiostatically discharged without hydrogen pressure to +350 mv vs. hydrogen potential.

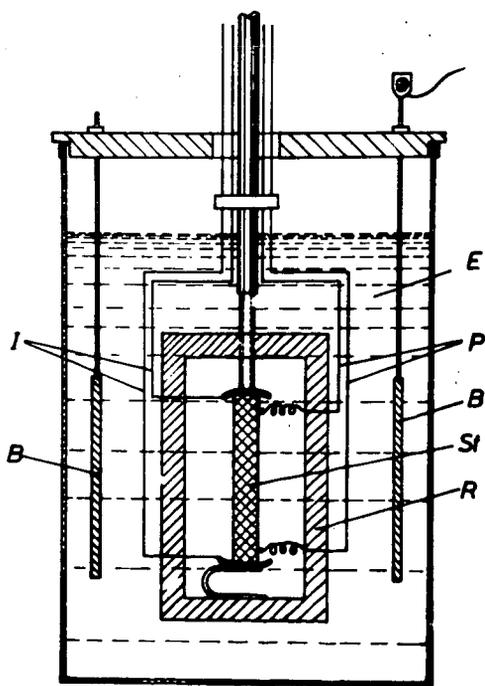


Fig. 6. Schematic arrangement for simultaneous measurement of electrical resistance, potential and weight of a Raney nickel specimen St as function of state of oxidation.

I current contacts,
P potential contacts,
E electrolyte 6 n KOH,
B cylindrical counter electrode.

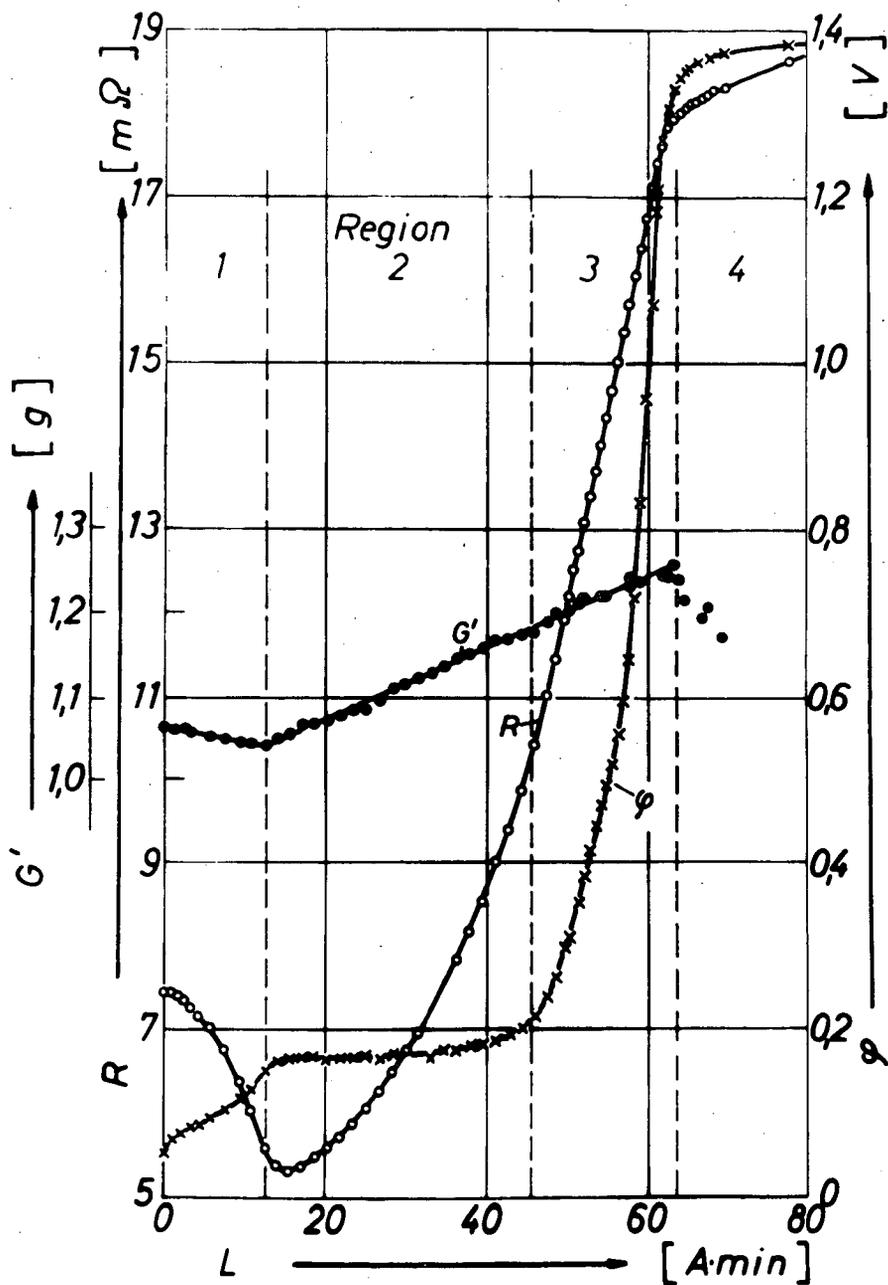


Fig. 7. Electric resistance R , potential φ in 6 n KOH against hydrogen reference electrode in the same electrolyte and apparent weight G' of a Raney nickel specimen St vs. its anodic charge L .

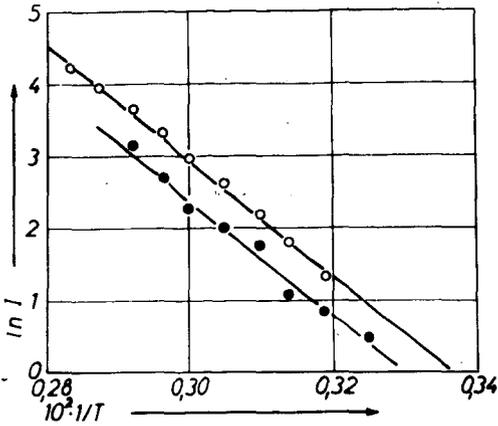


Fig. 8. Electrochemical reduction of oxidized Raney nickel as a function of the temperature T °K of electrolyte. I potentiostatic reduction current.

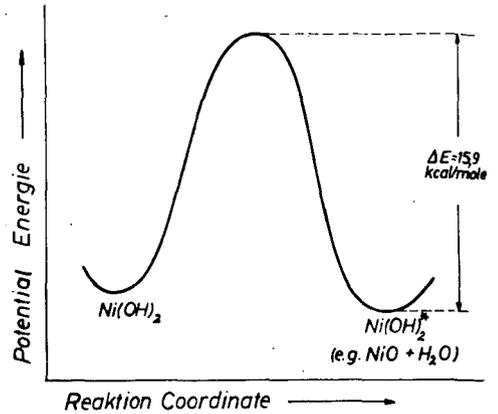


Fig. 9. Schematic of transformation of primary nickelhydroxide into the aged phase. Potential energy E vs. reaction course.

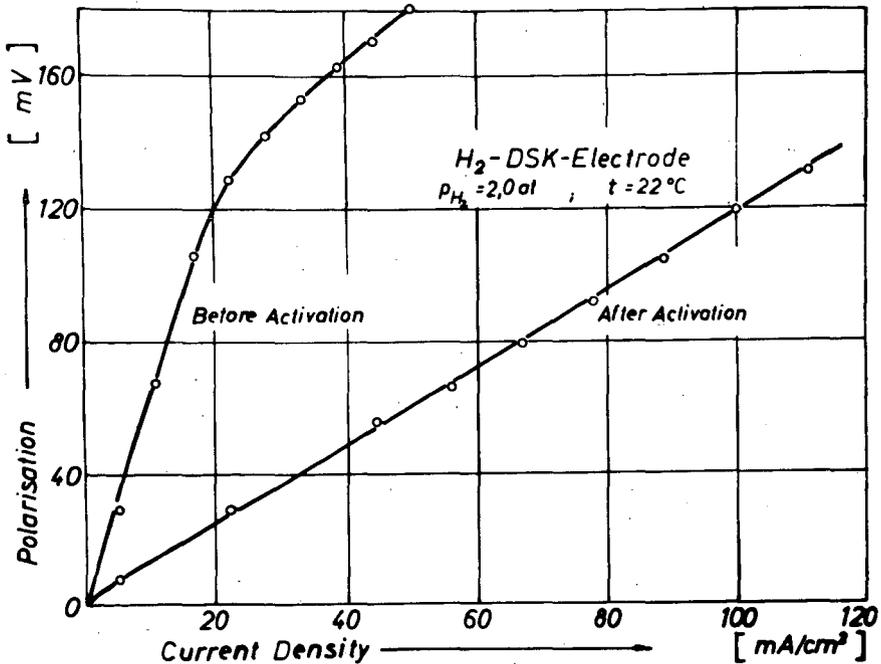


Fig. 10. Performance of a Raney nickel DSK anode showing the improvement after transient oxidation. Upper curve before, lower curve after transient oxidation and reduction.