

## STUDY OF FUEL CELL HYDROGEN DIFFUSION ANODE

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The electrochemical oxidation of a hydrogen diffusion anode with an inactivated nonpyrophoric nickel skeleton catalyst during withdrawal of current without hydrogen supply was studied. The behaviour of active and inactive electrodes with different sorts of catalysts at an overvoltage of up to 0.3 V was compared. An inactive electrode did not contain oxidizable hydrogen whereas the content of hydrogen in an active electrode was characterized by the atomic ratio  $H/Ni = 0.095$ .

During a study of alkaline hydrogen-oxygen cells we investigated in detail the catalytic properties of Raney nickel. Our previous work<sup>1</sup> dealt with the activation of the catalyst, its oxidation at positive potentials and regeneration. It is of interest to study the behaviour of the hydrogen anode during current load without hydrogen supply at a small polarization since the nickel skeleton contains adsorbed hydrogen which can be oxidized if no hydrogen is fed to the electrode. The current can be then withdrawn and no unwanted deterioration of the catalyst takes place. In addition, the nickel can be oxidized to an easily reducible form in another polarization region enabling a further loading of the electrode without gas supply.

The present work deals with the behaviour of the anode under the mentioned conditions, which is closely related to the operation of fuel cells, especially to their possible damage and regeneration.

## EXPERIMENTAL

*Catalysts.* Ni—Al alloys of different chemical and structural composition were ground, fractionated, leached in 7M-KOH at 95°C and inactivated by neutralization with tartaric acid and washing with hot water<sup>2</sup>. The catalyst particle size was less than 40 μm. The relevant data are in Table I.

*Electrodes.* Sintered double-layer electrodes, 7.3 cm in diameter, consisted of a carbonyl nickel cover layer (thickness 0.7 mm, porosity 45%) and a catalytic layer of carbonyl nickel,  $3.15 \pm 0.25$  g Raney nickel and a filler (thickness 1.3 mm, porosity 65%). The pressing pressure was 1.5 Mp/cm<sup>2</sup>, the electrodes were sintered at 450°C in hydrogen atmosphere.

*The method of measurement.* The electrodes were measured at 95, 70, 50 and 30°C in a half-cell arrangement with a Ni counter electrode in 7M-KOH separated by a ionically conductive separator. The gas overpressure was 0.7 atm. The electrode potentials are referred against a Hg/HgO reference electrode in the same electrolyte at ambient temperature. Galvanostatic curves were measured at a current density of 50 mA/cm<sup>2</sup>; first the electrodes were loaded with current under gas pressure until a constant potential was reached, then the gas supply was stopped and the gas

pressure was made equal to atmospheric so that the electrode became flooded. The measurements were performed after at least twenty-hour activation of the electrode and at least three-day measurement of electrochemical parameters.

TABLE I

## Basic Characteristics of Alloys and Catalysts

The differential specific polarization resistance,  $R_s$ , is a measure of the electrochemical activity.

Alloy type	Catalyst type	Alloy % Ni	Catalyst comp., %		Part. size of alloy $\mu\text{m}$	Surf. area of cat. in electr. $\text{m}^2/\text{g}$	$R_s$ $\Omega \text{cm}^2$		
			Ni	Al			95°C	70°C	50°C
VUK-67	R—Ni 3		68.2	3.8	—20	65	0.37	0.52	0.80
50/50	R—Ni 4	47.4	65.6	5.4	—20		0.36	0.58	0.83
	R—Ni 30		72.9	2.8	—40	50	0.43	0.92	1.13
	R—Ni 7		68.5	3.6	—25		0.51	0.83	1.23
KOM-68	R—Ni 8.12		62.3	6.0	—25	110	0.54	0.93	1.25
	R—Ni 26		76.6	2.0	0—6	45	0.66	0.95	1.48
	R—Ni 27	51.5	80.4	2.0	2—10	30	0.50	0.65	1.21
	R—Ni 28		81.6	1.7	5—20	35	0.64	1.10	1.35
	R—Ni 29		78.4	2.0	15—30	35	0.64	1.14	1.52
VUK-68	R—Ni 9	50.0	70.7	4.5	—40	80	0.64	1.18	1.57
50/50									
VUK-68	R—Ni 10	31.9	75.4	2.1	—40	40	0.65	1.14	1.81
30/70									
VUK-68	R—Ni 11	69.8	67.2	25.5	—40	20	1.04	1.62	2.65
70/30									
VUK-68	R—Ni 13	31.9	78.3	3.4	—40	18	0.64	1.26	1.81
30/70 T									
VUK-69	R—Ni 14.16	48.8	67.3	4.9	—20	95	0.35	0.51	0.72
49/49/2 Ti	R—Ni 15.17		65.8	4.8	—40	65	0.53	0.92	1.52
VUK-65	R—Ni 5.6	48.8			—20		0.25	0.40	0.51
50/50	R—Ni 31	48.8			—40		0.41	0.76	1.34
MCHZ	R—Ni 33	33.6	74.7	2.8	—40		0.47	0.62	0.96
66/34									

## RESULTS AND DISCUSSION

## ACTIVE ELECTRODE

*Galvanostatic curve.* When the activated (in contact with hydrogen in KOH solution at elevated temperature) anode fed with hydrogen is loaded with current the overvoltage depends on the catalyst activity, electrode structure and current density. With a good catalyst and porous system the overvoltage remains constant under normal operating conditions for several thousand hours. The polarization curve is linear up to relatively high current densities and does not indicate changes due to oxidation of nickel.

If, however, the active electrode is polarized anodically without supply of hydrogen, the galvanostatic curve shows two regions, A and B (Fig. 1). According to various

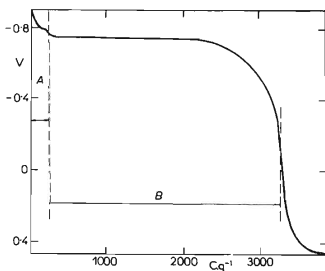


FIG. 1

Galvanostatic Curve of Hydrogen Diffusion Electrode with Nickel Skeleton Catalyst  
Current density  $50 \text{ mA/cm}^2$ .

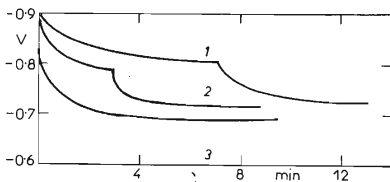


FIG. 2

Beginning of Galvanostatic Curve Corresponding to Hydrogen Oxidation  
Current density: 1 25; 2 50; 3 100  $\text{mA/cm}^2$ .

authors<sup>3-14</sup>, hydrogen oxidation takes place at 0.2–0.4 V, oxidation of nickel to Ni(II) at 0.4–1.4 V and oxidation of Ni(II) with oxygen evolution at still more positive potentials. In Fig. 2 is shown the influence of current density (and polarization) on the course of the first step and the possibility of evaluating the region corresponding to oxidation of hydrogen.

From several tens of curves for electrodes differing by their activity<sup>20</sup> the regions of the corresponding changes for the inactivated nickel catalyst were determined. The first change is finished at a polarization of 170–190 mV (at 50 mA/cm<sup>2</sup>), the second one takes place at 220–220 mV and the third at 1360 mV. These potentials do not change appreciably with different catalysts.

### *Influence of Aluminium*

After leaching the Raney alloy, a certain amount of aluminium remains in the catalyst grains. A study of the kinetics of leaching<sup>15</sup> showed that the residual content of Al was about 5% (leaching at 90°C or more) present prevalingly in the insoluble  $\delta$ -NiAl form<sup>8</sup>. The residual Al may be oxidized anodically at the potential of hydrogen oxidation as pointed out by several authors who concluded that for this reason the adsorbed hydrogen cannot be determined electrochemically<sup>8,12,17,18</sup>.

A detailed study of changes of the Al content in the electrode showed that a fraction of Al passed into the solution mainly during the time when the electrode was

TABLE II  
Course of Additional Al Dissolution from Electrodes

Electrode catalyst	R—Ni 9	R—Ni 14	R—Ni 11
Al-orig. cont., mg	49.3	56.2	284.7
Al-free diss., mg <sup>a</sup>			
3 h	27.8	24.1	12.3
2 h	11.9	3.6	—
24 h	3.2	18.7	5.9
24 h	1.7	1.2	—
24 h	0.2	—	—
Al-anod. diss., H <sub>2</sub> , mg <sup>b</sup>	0.3	0.2	0.1
Al-anod. diss., mg <sup>c</sup>	0.05	0.02	0.04
Al diss., mg (%)	45.2	47.8	18.3
	(92.4)	(85.0)	(6.4)

<sup>a</sup> Al dissolved during electrode standing idle in 7N-KOH at 90°C; <sup>b</sup> Al oxidized anodically at 60 mV polarization for 4 hours at 90°C with hydrogen supply into the electrode; <sup>c</sup> Al oxidized anodically at 320 mV polarization for 2 h at 90°C without hydrogen supply.

idle, the remainder during several hours after switching on the current. Some illustrative data are in Table II; it is seen that in our experiments the total oxidizable Al was removed prior to galvanostatic measurements. Some further evidence for this conclusion is given below.

### *Influence of Catalyst*

With a number of electrodes differing by their activity, the galvanostatic curves did not change if both the content of catalyst in the active state and the polarization current were constant (Fig. 1). Occasional deviations were caused by experimental errors. The first step, oxidation of hydrogen, corresponds to a specific charge of 156 C/g of catalyst, the second step,  $\text{Ni} \rightarrow \text{Ni(II)}$ , 3280 C/g (average from 37 measurements on 22 catalyst samples). The deviations are related neither to the content of residual Al nor to the surface area of the catalyst. A larger deviation occurred only with a catalyst denoted as R—Ni 11 with 25.5% Al prepared from the difficultly soluble  $\delta$ -NiAl alloy (70% Ni): the specific charges of the first and second step were only 56 and 359 C/g. It was shown<sup>16</sup> that electrodes with this catalyst were little active electrochemically implying adsorption of hydrogen even on the surface of slightly etched catalyst grains as confirmed in the present work. It follows further that Al from  $\delta$ -NiAl is not appreciably oxidized anodically at polarizations up to 190 mV (Table II) since only 7% of the total Al passed into the solution.

### *Content of Oxidizable Hydrogen*

The operating layer of the sintered nickel electrode contains besides catalytic also carbonyl nickel powder (from which also the cover layer is made). During activation of the electrode<sup>1</sup> the surface oxide layer on the carbonyl nickel is changed to metal of a fine structure resulting in an increase of the specific surface area of the carbonyl nickel. It is of interest to determine the fraction of adsorbed hydrogen bound to either type of nickel.

If the operating layer is made only from carbonyl nickel with the same system of gas pores then in the presence of hydrogen a potential close to the equilibrium hydrogen potential is attained. However, under current load without hydrogen supply the electrode potential is immediately shifted to more positive values (Fig. 3, curve 1), hence the electrode contains no nickel in the form capable of hydrogen adsorption. The stationary potential of the electrode, which was not in contact with hydrogen, corresponds to the  $\text{Ni}/\text{Ni(OH)}_2$  system and is shifted rapidly under current load into the region of oxygen evolution (Fig. 3, curve 2). Thereby it is proved that hydrogen in an active electrode is bound only to the nickel catalyst.

The question about the ratio of the bound hydrogen to the nickel catalyst is hitherto open although it has been the subject of many studies<sup>19</sup>; the ratio H/Ni was found to vary between 0.1 and 2.0. The character of the Ni—H bond is also not clearly defined: a part of the hydrogen is assumed to be adsorbed on the surface and the remainder absorbed in the bulk of the metal.

Analyses were performed mostly by the method of hydrogenation of organic compounds or thermal desorption; several authors used the electrochemical method, as a rule on activated catalysts, and one work was devoted to such measurements on a chemically inactivated catalyst incorporated into an electrode<sup>23</sup>.

In our case, we found the ratio  $H/Ni = 0.095 \pm 0.007$  (based on the average content of the catalyst in the operating layer) independent of the polarizing current and operating layer thickness and in good agreement with the value 0.084 in ref.<sup>23</sup>. A freshly leached catalyst<sup>8</sup> gave  $H/Ni = 0.3$ . The difference is due apparently to changes during inactivation (irreducible oxides) and manufacture of the electrodes (decrease of the surface area<sup>20</sup>). It seems that no distinct correlation exists between the content of oxidizable hydrogen and electroactivity of the catalyst or electrode except for the strongly different catalyst from the  $\delta$ -NiAl alloy (70% Ni), for which  $H/Ni = 0.02$ .

Provided that the coverage of the true surface area of the catalyst is equal to 1, desorption of  $H_2$  from  $1 \text{ cm}^2$  requires<sup>21</sup>  $2.18 \cdot 10^{-4} \text{ C}$  equivalent to  $2.27 \cdot 10^{-9} \text{ g H}_2$ . If one H atom is bound to one Ni atom and if the Ni surface is fully covered with hydrogen then after another reference<sup>22</sup> 1 ml  $H_2$  occupies  $3.64 \text{ m}^2$  of the true surface area of Ni, or  $1 \text{ cm}^2$  surface area binds  $2.42 \cdot 10^{-9} \text{ g H}_2$ . From these data, the specific surface area of the catalyst in our electrodes was calculated to be  $67.5 \text{ m}^2/\text{g}$ ; direct measurements by the BET method<sup>20</sup> gave  $60 \text{ m}^2/\text{g}$  on the average. In view of experimental errors the agreement is remarkable, an indirect evidence for the found content of hydrogen.

### Region of Nickel Oxidation

The length of the second step on the galvanostatic curve determined the charge due to the process  $Ni \rightarrow Ni(II)$ , namely  $3280 \text{ C/g}$ , which contributes to the electrochemical capacity of the electrode. It was already stated<sup>1</sup> that the oxidation involves both the catalytic and carbonyl nickel. Oxidation proceeds on the surface, but no correlation between the BET surface area or electrochemical activity of the electrode and the charge consumed in the second step was found with the studied group of catalysts.

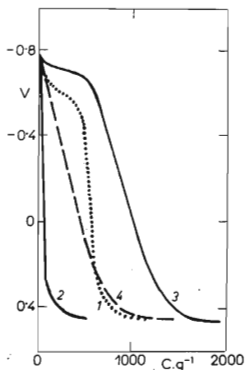


FIG. 3  
Galvanostatic Curves of Different Electrodes  
1 Only from carbonyl nickel, activated; 2 only from carbonyl nickel; nonactivated; 3, 4 nonactivated electrodes with a satisfactory catalyst;  $i = 50 \text{ mA/cm}^2$ .

### Influence of Temperature

With decreasing temperature the observed changes become undistinct<sup>12</sup> and overlap. In accord with the known influence of decreasing temperature on the electrochemical activity of the electrode, the electrode potential (under hydrogen supply), *i.e.* the starting voltage of the galvanostatic curve decreases gradually. Also, both delays on this curve become shorter and their corresponding overvoltages increase. The electrochemical capacities  $Q_H$  and  $Q_{Ni}$  due to oxidation of hydrogen and nickel depend on temperature as follows:

$t, ^\circ\text{C}$	95	70	50	30
$Q_H, \text{C/g}$	156	154	113	(28)
$Q_{Ni}, \text{C/g}$	3 280	2 420	1 100	(285)

The drop of the content of oxidizable hydrogen with decreasing temperature is considerable<sup>16</sup>. However, the data for the first step at decreasing temperature are only rough owing to errors of measurement.

### INACTIVE ELECTRODE

We shall consider an electrode that has not come into contact with hydrogen in the electrolyte so that the surface oxide layer on the catalyst is not reduced. Such an electrode can contain only the hydrogen which remained after inactivation. However, its stationary potential, about  $-0.77 \text{ V}$ , is close to the potential of the  $\text{Ni/Ni(OH)}_2$  system. The galvanostatic curve shows a delay corresponding to oxidation of Ni to Ni(II); this delay is more or less developed and sometimes even absent (Fig. 3, curves 3 and 4).

In the region of the first step an abrupt change is apparent, an evidence that the electrode catalyst does not contain any oxidizable hydrogen (and does not adsorb hydrogen during heating in hydrogen atmosphere). The course of the curve indicates that the residual aluminium is not oxidized either, hence a further evidence for the mentioned conclusions concerning the behaviour of aluminium.

Only those catalysts can be oxidized electrochemically which were not completely inactivated during their pretreatment. Differences in the depth of oxidation during inactivation are not manifested, *e.g.*, in the stationary electrode potential, but even the length of the second delay for electrodes with identical catalysts showed no correlation with the active and inactive states of the catalyst. Differences in the course of the curves indicate that the surface need not be attacked to the same depth during inactivation even though other properties of the catalyst are identical. Similar to the active state, also the inactive electrode with the R—Ni 11 catalyst behaves differently: its potential is shifted abruptly to positive values as soon as the current is switched on;

even the delay due to oxidation of Ni does not appear. This again shows that aluminium from  $\delta$ -NiAl is not oxidized electrochemically.

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