

HYDROGEN OVERTVOLTAGE IN CONCENTRATED SOLUTIONS OF SODIUM HYDROXIDE*

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The overvoltage of hydrogen was measured on four sorts of graphite and on a TiC-Ni mixture (*i.e.* on materials suitable for amalgam decomposer beds) in solutions of 20–40 wt.% NaOH at 60–90°C and current densities up to 1 A/cm². Measurements were performed in technically pure as well as in electrolytically purified solutions of NaOH.

The present work is a part of a series dedicated to the problem of decomposition of sodium amalgam — a basic reaction in the production of NaOH by the amalgam method. The kinetics of the decomposition^{1,2} can be evaluated from thermodynamic data³ and from the measurements of hydrogen overvoltage on materials used as decomposition catalysts.

The overvoltage, η_K , due to evolution of hydrogen on graphite electrodes in 5–50 wt.% NaOH was studied by many authors^{4–11}. Typical values of the Tafel constants, a_T and b_T , for the equation

$$\eta_K = a_T - b_T \log |i_K| \quad (1)$$

are summarized in Table I. The current density, i_K , of hydrogen evolution is referred to the geometric surface area of graphite. The cathodic overvoltage as well as the cathodic current are conventionally taken as negative. In the same table also the cathodic transfer coefficient, β , calculated from the equation¹²

$$\beta = 2.303RT/b_T F \quad (2)$$

is given. The absolute value of η_K in concentrated NaOH solutions decreases with increasing temperature (Table I). The concentration overvoltage is under these conditions negligible¹³ since the electrolyte is intensively stirred at the electrode surface by hydrogen bubbles^{14,15}. The value of η_K is according to Hine and coworkers⁸ practically independent of the electrolyte concentration in the range 10–50% NaOH, whereas Volkov⁶ reported a significant dependence: the absolute values of η_K at 70°C and 0.3 A/cm² were 0.95, 0.91, 0.75, 0.65 and 0.59 V in 10, 20, 30, 40 and 50% NaOH. This observation is in accord with the results of Burian¹¹ and Eriksson⁷ (Table I).

* Part VIII in the series Flow Electrolyzers; Part VII: This Journal 38, 2828 (1973).

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TABLE I
 Constants of Tafel Equation (I) for Hydrogen Overvoltage on Graphite

Ref.	$t, ^\circ\text{C}$	Conc. % NaOH	Range of i_K A/cm ²	$-a_T$ V	b_T V	β
5	40	40	0.001—0.3 ^a	0.671	0.148	0.420
	60	40	0.001—0.3	0.665	0.167	0.396
	80	40	0.001—0.3	0.617	0.160	0.438
6	25	27	0.1 —1	0.750	0.090	0.657
	80	27	0.1 —1	0.550	0.130	0.539
7	20	4	0.01—0.1	1.027	0.186	0.313
	20	23.8	0.01 —0.1	1.015	0.171	0.340
	80	4	0.01 —0.1	0.847	0.142	0.493
	80	23.8	0.01 —0.1	0.831	0.162	0.433
8	60	40	0.002—0.05	0.570	0.140	0.472
	80	40	0.002—0.05	0.515	0.140	0.500
10	20	44.3	0.001—1	0.672	0.148	0.393
11	90	10	0.05 —1	0.560	0.155	0.465
	90	20	0.05 —0.4	0.445	0.100	0.721
	90	20	0.4 —1	0.530	0.285	0.253
	90	30	0.05 —1	0.520	0.110	0.655
	90	40	0.05 —1	0.480	0.095	0.758
	90	50	0.05 —1	0.480	0.095	0.758

^a Elektrokohle Lichtenberg graphite (in other papers the sort of graphite unspecified).

EXPERIMENTAL

Apparatus

Graphite electrode 1 (Fig. 1) was fastened by means of a Teflon flange 8—11. The electrode was prepared so that the graphite sample (cylinder, sphere or plate) was provided with two isolated nickel wires serving as current lead and for measurement of electrode potential, embedded in poly-(methylmethacrylate) in an organic glass tube, ground planely together with the tube end, and polished with a metallographic paper No 0. Samples of graphitized fabric with current leads were fastened as shown in Fig. 2. The specification of the graphite samples under study is given in Table II. Platinum anode 2 was located in the narrower middle channel. The anode and cathode compartments were separated from each other by a glass frit sealed in glass tube 14. Mercury(II) oxide reference electrode 5 was inserted through ground glass opening 6 into the proximity of the graphite electrode. The reference electrode was provided with a Luggin capillary. The mutual position of the latter and graphite could be adjusted by axial motion of the graphite electrode in the flange as well as by rotating the HgO electrode in the ground glass joint 6. Hydrogen was fed into the apparatus through opening 3, whereby a circulation of the electrolyte was effected ensuring constant temperature and concentration in the cathode compartment. The hydro-

gen was purified by 5% KMnO_4 , 40% NaOH and on a Cr-Ni catalyst at 190–200°C. The apparatus was tempered by means of thermostated mantle pieces 7 and the temperature was measured by a thermometer inserted through ground glass opening 4.

Electric Circuit

A common three-electrode system was formed by indicator (graphite), auxiliary (Pt) and reference (HgO) electrodes (Fig. 3). A d.c. transistor power supply of the type TR-9252 (Orion, Hungary) was adapted as a galvanostat. The ohmic potential drop between the tip of the Luggin capillary and the graphite electrode was measured by the method of current interruption. The current was interrupted ten times per second for 100 μs by a transistor switch connected between the indicator and auxiliary electrodes. The switch was controlled by negative pulses (with a rise time shorter than 7 μs) from a precise astable multivibrator. Changes of the electrode potential caused by interrupting the current were followed on an oscilloscope; the voltage drop between the electrode and the Luggin capillary was read off as a change of the electrode potential immediately after current interruption with a precision of 5–10 mV at current densities lower than 1 A/cm^2 . At higher current densities, the precision was lower and was estimated to several tens mV.

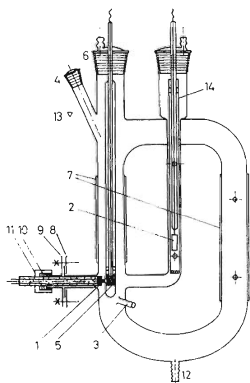


FIG. 1

Apparatus for Measurement of Hydrogen Overvoltage

1 Graphite cathode; 2 platinum anode; 3 hydrogen inlet; 4 ground glass opening for thermometer; 5 reference electrode; 6 ground glass stopper with opening for gas outlet; 7 thermostated mantle pieces; 8–11 combined flange; 12 outlet; 13 level of electrolyte; 14 glass tube ended with glass frit.

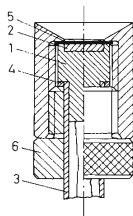


FIG. 2

Graphitized Fabric Electrode

1 Nickel support; 2 Teflon disc; 3 organic glass tube; 4 gasket; 5 graphitized fabric; 6 organic glass nut.

Solutions

The overvoltage of hydrogen was measured in solutions of NaOH of technical purity as well as in solutions purified electrolytically. A solution containing about 42% NaOH + 0.2% Na₂CO₃ was taken from the outlet of an industrial amalgam decomposer. (The same solution was used also in measuring the kinetics of amalgam decomposition in laboratory decomposers^{1,2}.) Preelectrolysis of the electrolyte was performed in vessels of 2 l holding capacity with nickel electrodes of 190 cm² surface area. A current of 3 A passed for about 150 h, *i.e.* the charge consumed was about 225 Ah per liter of electrolyte.

Method of Measurement

After filling the apparatus and the reference electrode with the electrolyte and tempering, the graphite electrode was polarized with a current density of 0.7 or 1 A/cm² for 3–6 h. When the

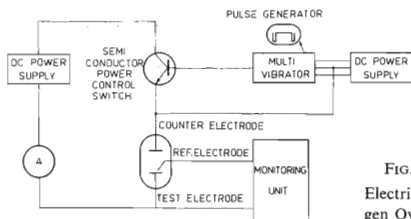


FIG. 3
Electric Circuit for Measurement of Hydrogen Overvoltage

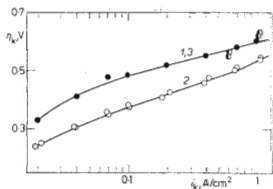


FIG. 4

Dependence of Hydrogen Overvoltage on Current Density

Tohoku Carbon graphite, 80°C. 1 Electrode No 1, 37.4% NaOH of technical purity; 2 electrode No 2, 43.2% NaOH preelectrolyzed; 3 electrode No 2, 43.2% NaOH of technical purity.

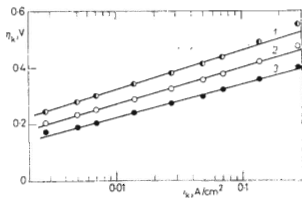


FIG. 5

Dependence of Hydrogen Overvoltage on Current Density

Elektrokohle Lichtenberg graphite, 22% NaOH of technical purity. 1 20°C, 2 50°C, 3 90°C.

graphite was ground prior to measurement, the potential decreased during polarization slowly by up to 200 mV with a simultaneous loosening of graphite particles from the electrode surface and pores. After the potential reached a stationary value, the measurement was started. At other current densities, the equilibration of the potential value took not more than 45 min. Measurements were performed in the order of increasing as well as decreasing current densities for every concentration and temperature several times. The measured potential difference between the cathode and reference electrode (corrected for iR drop in the electrolyte) was converted to overvoltage of hydrogen by subtracting the reversible potential, U_r , of the cell $\text{Pt, H}_2 | \text{NaOH}(c) | \text{HgO} | \text{Hg}$. The values of U_r' for the given concentration and temperature of the electrolyte were cal-

TABLE II
Properties of Cathode Materials Studied

Material	Manufacturer	Specification
Graphite	Elektrokohle Lichtenberg, GDR	plates designed for electrolysis of NaCl in amalgam electrolyzers, porosity 27–28%, contg. 10 p.p.m. V
Graphite	Tohoku Carbon Co., Japan	balls of 10 mm diam. for tower amalgam decomposers, contg. 97–98% C, 1.2–2.5% ashes, 20–50 p.p.m. V, activated with FeCl_3
Graphitized fabric	Société Carbon, Lorraine, France	designed for fuel cell electrodes, trade mark TGM 285 ₂ , thickness 0.6–0.7 mm, 1 m ² weighs 200–250 g, 0.1–0.2% ashes
Graphitized fabric	Nippon Carbon Co., Japan	designed for absorber beds, trade mark Carbon A, thickness 0.7 mm, 1 m ² weighs 200 g
TiC—Ni	Institute of Inorganic Chemistry, Czech. Acad. Sci., Prague	cylinders of composition 97% TiC + 3% Ni, diameter 6 mm, height 8 mm

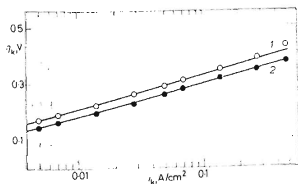


FIG. 6
Dependence of Hydrogen Overvoltage on Current Density
Elektrokohle Lichtenberg graphite, 43% NaOH of technical purity. 1 70°C, 2 90°C.

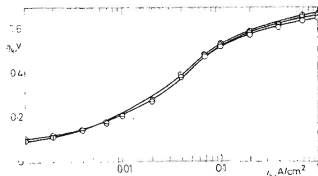


FIG. 7
Dependence of Hydrogen Overvoltage on Current Density
Tohoku Carbon graphite, 20% NaOH of technical purity. ⊕ 60°C, ⊖ 70°C, ○ 80°C.

culated from the equations given in the preceding communication³. From the dependences of η_K on cathodic current density i_K , the Tafel constants a_T and b_T were determined graphically; their averaged values with the corresponding range of current densities are given in Table III along with the transfer coefficient β from Eq. (2), logarithm of the formal exchange current density,

$$\log i_0 = a_T/b_T, \quad (3)$$

and activation energy for hydrogen evolution (at zero overvoltage), W_0 , defined by the equation¹⁶

$$\partial \ln i_0 / \partial (1/T) = -W_0/R. \quad (4)$$

TABLE III
Results of Measurement

Specification of material	$t, ^\circ\text{C}$	Concn. % NaOH	Range of i_K A/cm ²	$-a_T$ V	b_T V	β	$-\log i_0$	W_0 kcal/mol
Elektrokohle	20	22 ^a	0.0007–0.14	0.595	0.138	0.421	4.303	
Lichtenberg	50	22 ^a	0.005–0.14	0.525	0.124	0.516	4.225	3.93
	90	22 ^a	0.007–0.275	0.444	0.119	0.607	3.743	
	70	43 ^a	0.002–0.275	0.442	0.122	0.557	3.616	
	90	43 ^a	0.007–0.275	0.413	0.117	0.614	3.519	2.77
Tohoku Carbon	60	20.09 ^a	0.1–1	0.669	0.118	0.560	5.670	
	70	20.09 ^a	0.1–1	0.663	0.118	0.577	5.621	3.26
	80	20.09 ^a	0.1–1	0.655	0.118	0.594	5.549	
	60	37.4 ^a	0.1–1	0.630	0.118	0.560	5.336	
	70	37.4 ^a	0.1–1	0.612	0.119	0.572	5.145	7.13
	80	37.4 ^a	0.1–1	0.604	0.119	0.589	5.073	
	70	43.2	0.1–1	0.558	0.149	0.457	3.745	10.8
	80	43.2	0.1–1	0.536	0.151	0.463	3.550	
	90	43.2	0.1–1	0.499	0.150	0.480	3.327	13.1
Société Carbon	70	43.8	0.2–1	0.557	0.140	0.486	4.121	24.5
	80	43.8	0.2–1	0.563	0.153	0.458	3.680	
	90	43.8	0.2–1	0.536	0.162	0.444	3.475	12.0
Nippon Carbon	70	42.1	0.2–1	0.450	0.149	0.457	3.020	10.8
	80	42.1	0.2–1	0.438	0.155	0.452	2.826	
TiC 97%, Ni 3%	70	42.2	0.1–1	0.376	0.141	0.483	2.667	7.16
	80	42.2	0.1–1	0.368	0.145	0.483	2.538	
	90	42.2	0.1–1	0.361	0.153	0.470	2.359	10.5

^a Technically pure soda lye; other solutions were purified by preelectrolysis.

DISCUSSION

The reproducibility of measurement of the polarization curves can be characterized¹³ with the use of the confidence limit of the determination of the Tafel constants. With the Elektrokohle Lichtenberg graphite the 95% confidence limit was ± 13 mV for a_T and ± 7 mV for b_T referred to the arithmetic mean values in Table III (from 4–7 polarization curves for every temperature and concentration).

The technically pure soda lye from the industrial decomposer of sodium amalgam contained about 1 p.p.m. mercury¹⁷. It is seen from Table III and Fig. 4 (Tohoku Carbon graphite) that purification of the soda lye by preelectrolysis results in a drop in overvoltage by 60–100 mV (at 0.1–1.0 A/cm²). Based on ref.¹⁷, it is probable that in the technically pure electrolyte the cathode becomes partially poisoned with mercury during the evolution of hydrogen.

The graphite used in amalgam decomposers can be regarded as a porous electrode; its porosity is 20–30% and specific surface area 0.4–2.0 m²/g. However, in view of the fact that the values of the transfer coefficient β (Table III) do not deviate significantly from 0.5 (a value typical for evolution of hydrogen on smooth electrodes¹⁸) it is probable that in the case under study the porosity of graphite does not play a large role. With increasing current load namely the fraction of current flowing in the pores of the electrode diminishes in favour of the current flowing on the outer surface; moreover the gas evolved during the electrode reaction causes a considerable increase of the effective electrolyte resistance (*i.e.* resistance of the gas–electrolyte mixture) in the pores¹⁹.

The temperature dependence of the value of η_K is illustrated by Figs 5–12 and can be also derived from Table III. The value of η_K decreases with increasing tempera-

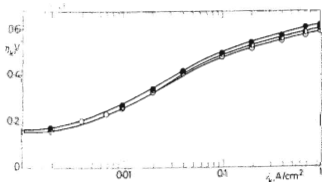


FIG. 8

Dependence of Hydrogen Overvoltage on Current Density

Tohoku Carbon graphite, 37.4% NaOH of technical purity. ● 40°C, ◐ 60°C, ○ 80°C.

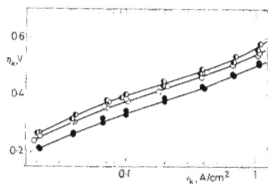


FIG. 9

Dependence of Hydrogen Overvoltage on Current Density

Tohoku Carbon graphite, 43.2% NaOH preelectrolyzed. ● 70°C, ○ 80°C, ◐ 90°C.

ture as characterized by the value of W_0 in Eq. (4) or by the quotient $\Delta a_T/\Delta t$ lying in the range 0.7–2.15 mV/°C.

The dependence of η_K on the concentration of NaOH is close to the theoretical one, which can be derived on the assumption that the rate-determining step in the evolution of hydrogen on graphite is the Volmer or Heyrovský reaction. In this case the following equation applies²⁰:

$$\eta_K = -(RT/\beta F) \ln |i_K| + (RT/F) [\ln (a_{OH^-} - p_{H_2}^{1/2}) + (1/\beta - 1) \ln a_{H_2O}] + \zeta + k_1, \quad (5)$$

where a_{H_2O} and a_{OH^-} denote activities and the constant k_1 involves all terms independent of the concentration of NaOH. The ζ potential can be neglected at the concentrations in question.

According to Eq. (5), the change of η_K with concentration at constant i_K and temperature is given by

$$\Delta \eta_K = (RT/F) [\Delta \ln a_{OH^-} + \Delta \ln p_{H_2}^{1/2} + (1/\beta - 1) \Delta \ln a_{H_2O}]. \quad (6)$$

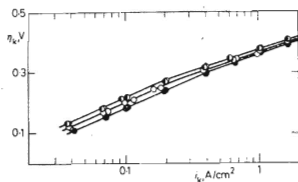


FIG. 10

Dependence of Hydrogen Overvoltage on Current Density

TiC-Ni electrode, 42.2% NaOH preelectrolyzed. ● 70 °C, ○ 80 °C, ● 90 °C.

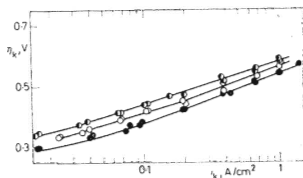


FIG. 11

Dependence of Hydrogen Overvoltage on Current Density

Société Carbon graphitized fabric, 43.9% NaOH preelectrolyzed. ● 70 °C, ○ 80 °C, ● 90 °C.

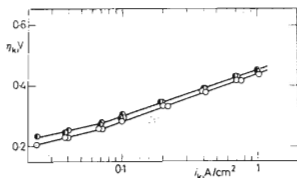


FIG. 12

Dependence of Hydrogen Overvoltage on Current Density

Nippon Carbon graphitized fabric, 42.1% NaOH preelectrolyzed. ● 70 °C, ○ 80 °C.

From this equation the theoretical values of Δa_T (i.e. differences of η_K at $i_K = 1 \text{ A/cm}^2$) were calculated for the ranges of 22–43% and 20.1–37.4% NaOH. The values of $\Delta \ln p_{\text{H}_2}$ and $\Delta \ln a_{\text{H}_2\text{O}}$ were calculated from the equations published previously³ at a total pressure of 1 atm. The values of $\Delta \ln a_{\text{OH}^-}$ were calculated from the differences of the reversible voltage of the amalgam-hydrogen cell, ΔU_r , at constant temperature, amalgam concentration and partial pressure of hydrogen:

$$\Delta U_r = (RT/F) \Delta \ln (a_{\text{NaOH}\pm}^2 / a_{\text{H}_2\text{O}}), \quad (7)$$

whence it follows (on the assumption that $a_{\text{OH}^-} \approx a_{\text{NaOH}\pm}$)

$$(RT/F) \Delta \ln a_{\text{OH}^-} = 0.5[\Delta U_r + (RT/F) \Delta \ln a_{\text{H}_2\text{O}}]. \quad (8)$$

Theoretical and experimental values of Δa_T are as follows:

Graphite	$t, ^\circ\text{C}$	Conc. range % NaOH	β	$\Delta a_T, V$ theor.	$\Delta a_T, V$ exper.
Elektrokohle	70	22–43	0.56	0.052	0.043
Lichtenberg	90	22–43	0.61	0.059	0.032
Tohoku	60	20.1–37.4	0.56	0.049	0.040
Carbon	80	20.1–37.4	0.59	0.048	0.051

The differences between theoretical and experimental values are comparable with the reproducibility of the determination of a_T . The dependence of the overvoltage of hydrogen on graphite on the concentration of NaOH (similarly as found by Eriksson⁷ and Burian¹¹) is intermediate between the pronounced decrease of the absolute value of η_K with increasing concentration found by Volkov⁶ and invariance of η_K with respect to concentration reported by Hine and coworkers⁸.

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