HYDROPHOBIC HYDROGEN ANODE WITH A NICKEL CATALYST

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A hydrophobic porous hydrogen anode was prepared whose electrochemical parameters are comparable with anodes containing a platinum catalyst. For its successful preparation, oxidation of the Raney nickel catalyst with air oxygen or with fluorine from Teflon must be prevented. The electrodes of a geometric surface area up to 450 cm^2 were tested in cells and modules filled with 7M-KOH.

The Raney nickel catalyst is often used in gas diffusion anode for fuel cells, where it was introduced toward the end of fifties[1]. Originally it was used in pressurized sintered electrodes[2-6] and latter in supported powder electrodes[7]. To hydrophobic electrodes, it was applied only rarely[8-10] since platinum was often used instead[11] even in alkaline medium. However, the use of Raney nickel should be preferred for economic reasons.

The present work brings some new results in this respect as a continuation of the preceding communication[12] devoted to the nickel catalyst.

EXPERIMENTAL

Materials

The operating layer of the electrodes contained: *a*) Raney nickel catalyst prepared by alkaline leaching of a Ni—Al alloy (1 : 1) and deactivation with 3% H_2O_2; its particle size after fractionating was 6 μm and 6—45 μm. *b*) Acetylene black P-1042 (Stickstoffwerke Piesteritz, GDR), pretreated in a mixer. *c*) Teflon dispersion GP 1 (ICI, England). *d*) Filler (NH_4HCO_3), fraction —45 μm.

The operating layer was prepared by mixing the components wetted with an excess of ethanol which was then sucked off, the mix was dried, kneaded with xylene, and rolled to form a 0·9 to 1·0 mm thick layer, from which the filler was removed by heating to 50°C on the air and the dispersing agent by heating to 210°C during sucking off with a water pump.

The cover layer was a microporous layer of Teflon and carbon black, whose mix was kneaded with the addition of xylene and rolled as desired.

The current collector was an iron net (ČSN 153 140) with 1·6 mm mesh size and 0·1 mm wire thickness, degreased in gasoline, pickled in diluted (1 : 1) hydrochloric acid at 60°C, rinsed and dried.

Preparation of Electrodes

The operating and cover layers prepared as indicated above were laid on each side of a collector (in a sandwich form) and hot-pressed, whereby the Teflon particles in each layer fused firmly together. To prevent oxidation with air, the electrodes were wrapped in a metal foil prior to pressing, which proceeded fo 3 min at 325°C and 3·62 MPa. After taking out of the press, the electrodes were cooled by inserting between two metal plates cooled with water.

Measurements

The electrochemical parameters were measured on disc-shaped electrodes of 10 cm^2 area in a half--cell arrangement without hydrogen overpressure; the electrolyte was 7M-KOH at 70°C, reference electrode Hg/HgO in the same solution. The electrodes were activated with hydrogen for 16 h at 70°C. The potential values were measured with a voltmeter of the type Solartron 7065 with an on-like calculator of the type HP 9820 A and a scanner of the type HP 3495 A. A d.c. power supply of the type HP 6002 A served as a source of current. The program for the measurement of the polarization curves was arranged so that the limiting voltage of a loaded electrode was −0·80 V.

RESULTS AND DISCUSSION

Semihydrophobic electrodes must be provided with a cover layer of a finely porous plastic material, which prevents the penetration of electrolyte even at an overpressure of 0·1 MPa, ensuring a rate of gas flow corresponding to current densities up to 0·1 A/cm^2.

Such diaphragms are usually prepared from fine Teflon particles. The Teflon diaphragms developed by us[13] were not suitable for anodes with a nickel catalyst, since the catalyst corroded during leaching out the filler (NaCl) by hot water, and when the filler was leached out beforehand, the porous structure was deteriorated during heat treatment of the electrodes. Therefore, we proposed a new type of PTFE diaphragm containing carbon black as filler, whose porous structure does not change even by hot pressing. It is characterized by the overpressure, $p_k = 0{\cdot}12$ MPa, necessary for penetration of water, and the velocity of flow of nitrogen, $U = 4 \,.\, 10^{-4}$ m/s at an overpressure of 0·002 MPa.

In preparing the electrodes, a heat tratment is indispensable; to prevent deterioration of the catalyst layer, the electrodes must be hot-pressed under exclusion of air and before the decomposition of Teflon commences. The Raney nickel is namely even in the inactivated form used very reactive against both oxygen and Teflon at elevated temperatures. The reaction is exothermic in either case and can eventually lead to destruction of the electrode. The reaction between nickel and Teflon starts at about 320°C, although according to catalogue data only a slight evolution of fluorine from Teflon takes place around this temperature. The decomposition of Teflon is apparently catalysed by nickel. This reaction cannot be prevented by an inert atmosphere.

The Operating Layer

Our attention was focussed on the optimisation of the operating layer. Its basic component is an inactivated Raney nickel catalyst prepared with regard to earlier findings[12]. The catalyst particle size was 6–45 μm; finer fractions gave essentially the same results, but their preparation was rather laborious, little effective, and the fine particles were apt to atmospheric corrosion. Therefore, coarser fractions were preferred.

Although carbon black has been used rather often as a component of operating layers, in our case its presence proved unfavourable, as is obvious from the values of the polarization resistance at different contents of carbon black (Table I). This can be attributed to two counteracting effects, namely the electronic conductivity and hydrophobicity of the carbon black. The latter effect prevents the electrolyte from contact with the catalytic grains and is obviously dominant, as can be judged from Table I. At the same time, it is evident that the optimum Teflon content in the operating layer is 10%.

The latter finding is documented graphically in Fig. 1, where the catalytic performance, α (A/g) is given by the current density at a chosen polarisation corresponding

TABLE I

Influence of composition of the operating layer on the polarization resistance

Content of C wt. %	Cont. of PTFE wt.%	Cont. of Ni mg . cm^{-2}	R_s ohm . cm^2
0	15	55	0·586
7·7	15	79	1·123
11	15	75	1·404
14·2	15	67	2·007
4	10	55	0·640
4	15	63	0·875
4	20	71	1·044
4	25	69	1·779
0	10	16	0·840
0	10	24	0·576
0	10	35	0·488
0	10	45	0·431
0	10	70	0·361
0	10	91	0·372
0	10	110	0·381

to an operating layer with a square density of the catalyst of $1/gcm^2$. The drop in the catalytic performance at a higher Teflon content is due to the rising content of hydrophobic pores hindering the electrolyte transport. A similar drop can be expected at low contents of PTFE, since the drowned pores hinder the gas transport.

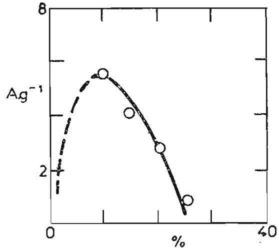

FIG. 1

Catalytic performance of hydrophobic anodes, α, as function of the PTFE content Q at 4% carbon black in the operating layer

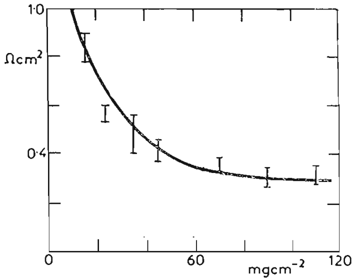

FIG. 2

Dependence of the polarization resistance of hydrophobic anodes on the catalyst square density, F, in the operating layer containing 10% PTFE

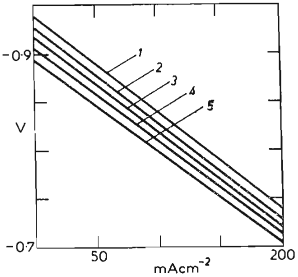

FIG. 3

Polarization curves for hydrophobic anodes with Ni catalyst at 70°C (15% PTFE and 4% carbon black in the operating layer). Concentration of KOH: *1* 9·6; *2* 8·2; *3* 7·1; *4* 6·5; *5* 5·2 mol/l

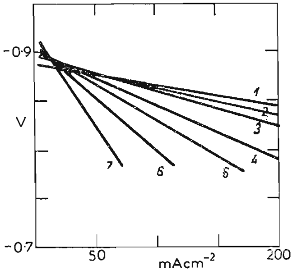

FIG. 4

Polarization curves for hydrophobic anodes with Ni catalyst at various temperatures (15% PTFE and 4% carbon black in the operating layer): *1* 90°C; *2* 80°C; *3* 70°C; *4* 60°C; *5* 50°C; *6* 40°C; *7* 30°C

Influence of the Catalyst Square Density

Different values of the square density can be achieved with layers of different thickness. This, however, brings about also differences in the structure of the operating layer as a result of different rolling conditions. Therefore, we prepared a base layer of 0·5 mm thickness and 16 ± 2 mg/cm^2 catalyst square density, and by assembling a chosen number of these layers together we obtained electrodes with square density of the catalyst up to 110 mg/cm^2. It follows from the polarization resistance (Table I), especially from its dependence on the square density (Fig. 2) that the lowest sufficient square density of the catalyst in the hydrophobic anode under study is about 40 mg . . cm^{-2}. Higher values bring no improvement since the positive effect of the higher catalyst content is outbalanced by the negative effect of worse transport conditions.

Influence of Electrolyte Concentration

According to theoretical calculations, increasing electrolyte concentration causes a moderate shift of the hydrogen electrode equilibrium potential to more negative values. However, the behaviour of the electrode under load is of more practical interest. The results for an anode containing 15% PTFE and 4% carbon black at 70°C are shown in Fig. 3. Changing electrolyte concentration from 9·6 to 5·2 mol/l does not cause a shift of the electrode potential at a current density of 0·1 A/cm^2 to values at which the oxidation of nickel takes place (*i.e.*, more positive than −0·76 V), hence the electrode cannot be damaged.

Influence of Temperature

Electrode of optimum composition were measured at 30−90°C. The decreasing temperature causes a moderate shift of the equilibrium potential of the anode to more negative values, however the polarization curves are negatively influenced as shown in Fig. 4; this is obviously caused by the decreasing exchange current density and conductivity of the electrolyte. The optimum operating temperature is 80−90°C. At 70°C, the preferred operating temperature, the current-voltage characteristic is only slightly worse. At temperatures above 70°C, there is a danger of spotaneous penetration of hydrogen through the electrode into the electrolyte[14].

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