THE SILVER CATALYST IN THE HYDROPHOBIC OXYGEN ELECTRODE

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Summary

Ten sorts of silver powder were tested as the catalysts for hydrophobic air electrodes in an alkaline electrolyte. The fine grain catalysts meet the demands of the electrodes better than the catalysts with large surface area which proved not to be satisfactory. The catalyst prepared by reduction of the aqueous suspension of a solid silver salt has the best properties. Electrochemical electrode behaviour is improved by using pure oxygen. The characteristics of some silver catalysts in hydrophilic electrodes were also determined.

Introduction

The prevailing losses of potential in electrochemical power sources operating with oxygen cathodes are caused by the high overpotential of oxygen electrodes. New effective electrocatalysts for oxygen reduction are looked for to meet the demand for higher current densities at low overpotentials [1, 2] especially in fuel cells operating with air electrodes. The application of air breathing hydrophobic air electrodes has supported these demands.

The range of choice of suitable catalysts for oxygen reduction is not great. The phthalocyanines [3 - 6] seemed to be promising in fuel cells with acid electrolytes, but up till now they have not fulfilled expectations. Platinum catalysts can be successfully used for both acid and alkaline electrolytes, but they are very expensive for commercial applications. From the economic point of view carbon and silver appear as the most suitable catalysts. Boron carbide [7] has also been investigated, but it exhibited low catalytic activity.

Silver in the form of fine powders is frequently used in the cathodes of fuel cells operating with an alkaline electrolyte. The silver catalyst gives relatively positive potentials to oxygen electrodes on account of its good activity for hydrogen peroxide decomposition.

The catalytic properties of silver in hydrophilic electrodes have been published in many references and silver powder has also been successfully applied in hydrophobic electrodes [8, 9]. Hydrophilic and hydrophobic electrodes differ in their structure and therefore a difference in the activity of the various silver catalysts can be expected [10].

This report deals with the effect of silver powders prepared in different ways on the quality of the oxygen cathode operating with air in alkaline electrolyte. In some cases the catalytic activity is compared in both the hydrophobic and hydrophilic types of electrodes.

Experimental

Catalysts

The conditions for the preparation of the catalysts together with their identification numbers are given in Table 1. The products prepared from aqueous solution were decanted, filtered, dried (378 K), carefully pulverized and sieved. The Ag-Al alloy was crushed, milled, leached, washed out and sieved. A screen with a mesh size of 40 μm was used for the final sieving in all these cases. Catalyst No. 9 is the industrially produced silver powder for Ag-Zn storage batteries.

TABLE 1

The methods of catalyst preparation

Catalyst No.	Method
	Reduction of a 5% ammoniacal AgNO$_3$ solution by means of:
1	NaBH$_4$ (295 K)
2	N$_2$H$_4$ (295 K)
3	Na$_2$S$_2$O$_4$ (295 K)
	Reduction of a 5% AgNO$_3$ solution by means of:
4	N$_2$H$_4$ (295 K)
5	NaH$_2$PO$_3$ (373 K)
6	C$_6$H$_4$(OH)$_2$ (295 K)
	Other methods:
7	thermal decomposition of (COOAg)$_2$
8	leaching of an Ag-Al alloy (65/35)
9	silver powder, Safina n.p.
10	reduction of a silver salt suspension

Electrodes

Three kinds of electrodes were examined. (a) The hydrophobic electrodes with a semi-hydrophobic active layer were prepared [11] from a mixture of

catalyst powder, PTFE dispersion and removable filler and treated by rolling onto the hydrophobic layer prepared from PTFE suspension and removable filler only [12]. These electrodes were not thermally treated. The removable filler leached out with hot water left a high porosity in the active, as well as in the cover, layer. (b) The sintered double layer hydrophilic electrodes having an active layer thickness of 1.3 mm, contained 27% Ag by weight and the rest formed from carbonyl nickel only. The porosity of the active layer was 71% with a pore diameter under 40 μm. The cover layer thickness of 0.7 mm was prepared from carbonyl nickel powder only. The layer porosity was 46% (by volume) and the pore diameter 1.5 μm. These electrodes were sintered at 723 K in a hydrogen atmosphere. (c) Unsintered supported double layer hydrophilic electrodes with the cover layer made of asbestos paper, had the active layer prepared from catalyst and PTFE (4% by weight) as a bonding agent. The active layer had a thickness of 1 mm and a porosity of 65% (by volume). The cover layer (asbestos paper) had a thickness of 0.4 mm with a porosity of 74% (by volume) and an average pore diameter of 2 μm.

Measurement

All the electrodes were prepared with a diameter of 40 mm and tested in the half-cell assembly against a Hg/HgO reference electrode in 7 N KOH. The hydrophilic electrodes operated with an oxygen overpressure 0.07 MPa. The hydrophobic ones operated without gas overpressure and the air was not purified from carbon dioxide. The active layer of the hydrophilic electrodes was in contact with the gas phase in contrast to the hydrophobic ones, where the active layer was on the electrolyte side.

The potentials E_i at a current density of 0.1 A/cm^2 or the current densities i_E at a potential of $-$ 0.2 V express the electrochemical activity of the silver catalysts embedded in the active layer of these electrodes.

Results and discussion

Hydrophobic electrodes

The silver catalyst is used in the form of finely dispersed particles in the active layer. Many ways of silver powder preparation have been described, as for instance the reduction from aqueous solutions of salts [13, 14], the thermal decomposition of silver salts [15 - 17] or leaching of silver alloys [18 - 20]. A very active catalyst may be obtained by the reduction of an aqueous dispersion of silver oxide [21].

Recently the members of the Institute of Physical Chemistry and Electro-chemistry of the Czechoslovak Academy of Science have been working on the preparation, and determination of the characteristics, of some silver catalysts [22] and have found that silver prepared by various processes of reduction from aqueous solutions had a surface area which varied only within a quite small range, from 1 to 6 m^2/g. Our results (Table 3) confirmed these data (none of silver powders exceeded this range) as well as agreeing with the few

values given in the literature [17, 23, 25]. The silver catalyst prepared from Ag–Al alloys had a maximum surface area of 10 m^2/g which is very different from that of the similar Raney nickel catalyst (100 - 200 m^2/g). The industrially produced silver powder (catalyst 9) has a very small surface area of 0.05 - 0.5 m^2/g.

The high polarization of an oxygen cathode is brought about by other causes in addition to the high activation polarization. The number of the chemisorption sites and the activation and reaction centres is small, which is caused by the small surface area of the Ag catalysts. There is therefore the question of whether a surface enlargement from 0.1 on 6.0 m^2/g could significantly influence the electrode activity.

Our long-term experiments confirmed that the replacement of catalyst 9 by the silver prepared directly by thermal decomposition of oxalate improved the electrochemical activity of the sintered oxygen electrodes. The higher activity was adjudged to result from the larger surface of silver catalyst. But it is well known [22, 23] that the surface of silver powder can be diminished at a temperature above 0.3 T_k (T_k is the melting point) which corresponds to 411 K. Catalyst quality cannot therefore be explicitly judged in sintered electrodes. In the last decade the technology of electrode preparation without thermal treatment has advanced [20]. The efficiency of silver catalysts can be much better compared in such electrodes. A more sensitive resolution can be achieved from the reduction of the oxygen partial pressure which can be determined at the air electrode. This method of catalyst testing requires the hydrophobic type of cathodes without thermal treatment with good mass transfer and electronic conductivity [24].

The data for all the electrodes tested, containing the same weight of the investigated silver catalyst per unit area, are given in Table 2. Variations in the thickness of the active layers and the amount of silver per unit area were caused by differences in the particle shape of silver and the specific weight of powders; that is by differences in the specific volume. Similarly a volume contraction took place after the leaching out of the filler from the active layers. Analysis of the effect on the basic characteristics showed that the above mentioned factors had no significant influence neither had the small differences in the porosity and the thickness of the hydrophobic cover layer [24].

The polarization curves of all the electrodes tested are shown in Figs. 1(a) and 1(b). From these Figures it follows that catalyst 10 proved to be the best and most effective and catalysts 2, 6 and 7 form the second best group, while the others were not satisfactory. Catalyst 9 produced industrially proved to be the worst of all.

An appreciable reduction in the polarization was achieved by supplying pure oxygen to these electrodes without overpressure. The results are given in the second part of Table 2. Comparing the results we can see that the sequence of the first three catalysts and the last one was identical in air and oxygen. The application of pure oxygen improved the performance of the best electrode, in terms of the current density i_E at $E = -0.2$ V, more than three fold. Oxygen increased the electrode activity by a factor of 2.4 on average.
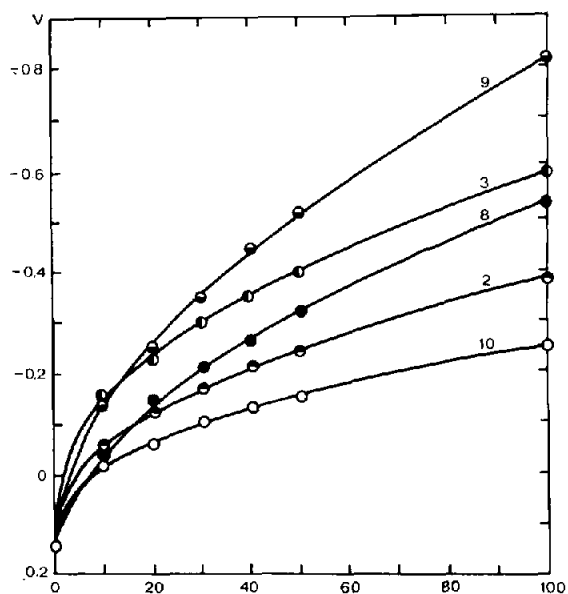
TABLE 2

Characteristics of the hydrophobic electrodes. Potential E_i (V) at the current density $i = 0.1$ A/cm^2. Current density i_E at the potential $E = -0.2$ V. Temperature 295 K

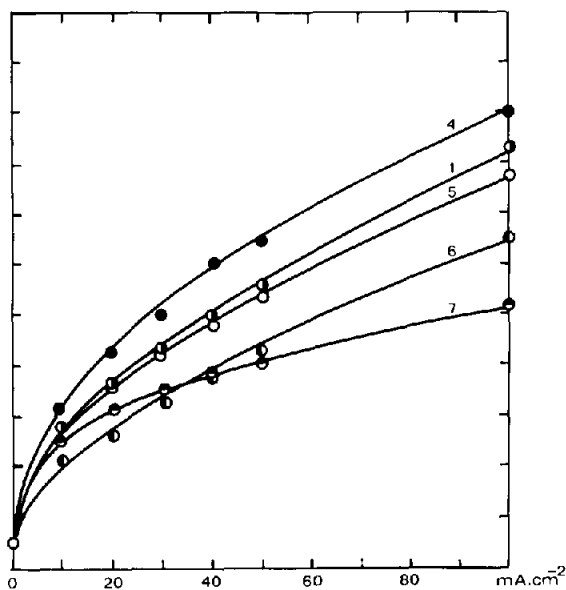| Catalyst No.	Thickness (mm)		Catalyst load (mg Ag/cm^2)	Porosity of the operating layer (% by vol.)	Electrochemical activity					
	Operating layer	Cover layer			Air			Oxygen		
					$-E_i$	i_E	Sequence	$-E_i$	i_E	Sequence
1	0.52	0.16	84	71	0.623	25	7	0.280	63	5
2	0.50	0.16	84	76	0.380	40	4	0.270	65	4
3	0.57	0.13	84	73	0.580	16	9	0.423	43	9
4	0.49	0.13	83	69	0.703	17	8	0.287	76	6
5	0.45	0.15	77	70	0.573	27	6	0.312	54	8
6	0.63	0.08	88	54	0.454	45	3	0.199	105	3
7	0.52	0.12	69	62	0.320	50	2	0.163	130	2
8	0.52	0.14	71	68	0.535	28	5	0.292	62	7
9	0.52	0.13	67	69	0.820	15	10	0.575	27	10
10	0.45	0.12	79	74	0.250	75	1	0.135	250	1

TABLE 3

Comparison of catalyst parameters

Sequence	Electrochem. charact. (see Table 2)		Surface area		Crystal size		H_2O_2 decomposition		Observed surface articul. (condition)
	air catalyst No.	oxygen catalyst No.	Catalyst No.	(m^2/g)	Catalyst No.	$(cm \times 10^{-6})$	Catalyst No.	(cm^3/min)	catalyst No.
1	10	10	8	5.81	8	1	10	15.3	8
2	7	7	1	5.71	1	2	6	11.7	1
3	6	6	10	3.38	2,3	3	5	8.6	10
4	2	2	2	1.53	2,3	3	7	7.2	3
5	8	1	3	1.51	4	4	8	6.5	5
6	5	4	4	0.69	5,10	5	1	5.8	7
7	1	8	7	0.68	5,10	5	2	4.7	4
8	4	5	5	0.66	7	8 - 10	4	4.2	2
9	3	3	6	0.42	6	20 - 100	3	3.4	6
10	9	9	9	0.21	9	> 100	9	3.1	9

Fig. 1. Polarization curves of air cathodes containing different kinds of Ag catalysts. (The identification of the catalysts is identical with Table 1.)

Evaluation of the catalysts

None of the physical–chemical experimental methods are suitable for the indirect determination of the catalyst capability to ionize oxygen. The

goal of these investigations was not to find such a method but only to evaluate the tested silver catalysts in several ways and to look for correlations in their behaviour in the hydrophobic electrode.

At first the particle size was studied as an important factor from the point of view of heterogeneous catalysis. Silver powder prepared in different ways usually had fine grains, but sedimentation analysis proved not to be a convenient means of grain size evaluation. Conglomerates and clusters of greater dimensions, which are in general difficult to disintegrate, are already formed during the preparation from aqueous solutions. On the contrary attempts to break these down may lead to compacting of the Ag clusters. Such powder materials behave quite differently from the sedimentation analysis aspect. The results for two typical catalysts (5 and 6) with different characteristics are demonstrated in Fig. 2. The former (5) formed great spongy conglomerates and the latter formed very fine particles. The size of particles was determined immediately after the preparation and then after sieving through a 40 μm sieve in the wet and dry state. The corresponding curves show the unsuitability of sedimentation analysis for these materials.
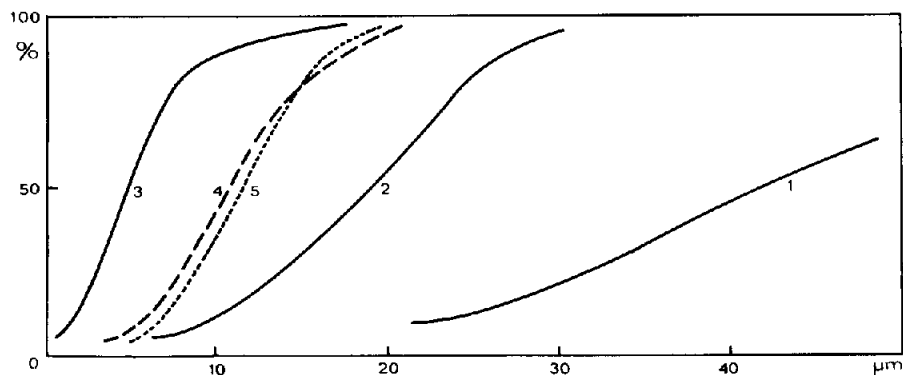

Fig. 2. Sedimentation analysis of two Ag catalysts. Catalyst 5: 1-wet after the preparation. 2-dried and sieved under 40 μm, 3-wet and sieved under 40 μm. Catalyst 6: 4-wet after the preparation. 5-dried and sieved under 40 μm.

The second possibility for the evaluation of the silver powder catalysts was surface measurement by the BET method. These results are given in Table 3.

The microphotographs were taken by means of a scanning electron microscope (Fig. 3) enabling the dimensions and shape of particles to be measured and compared. The grains of the catalysts were found out to have predominantly a very developed (articulated) surface and the particles had a spongy structure. Very rarely the grains had a simple shape (*e.g.* catalysts 6, 8 and 9).

The size of crystals was examined by means of RTG analysis and the results are given in Table 3. Catalysts 6 and 9 had coarse crystals in contrast to the others all of which had a similar crystal size of the order 10^{-6} cm.
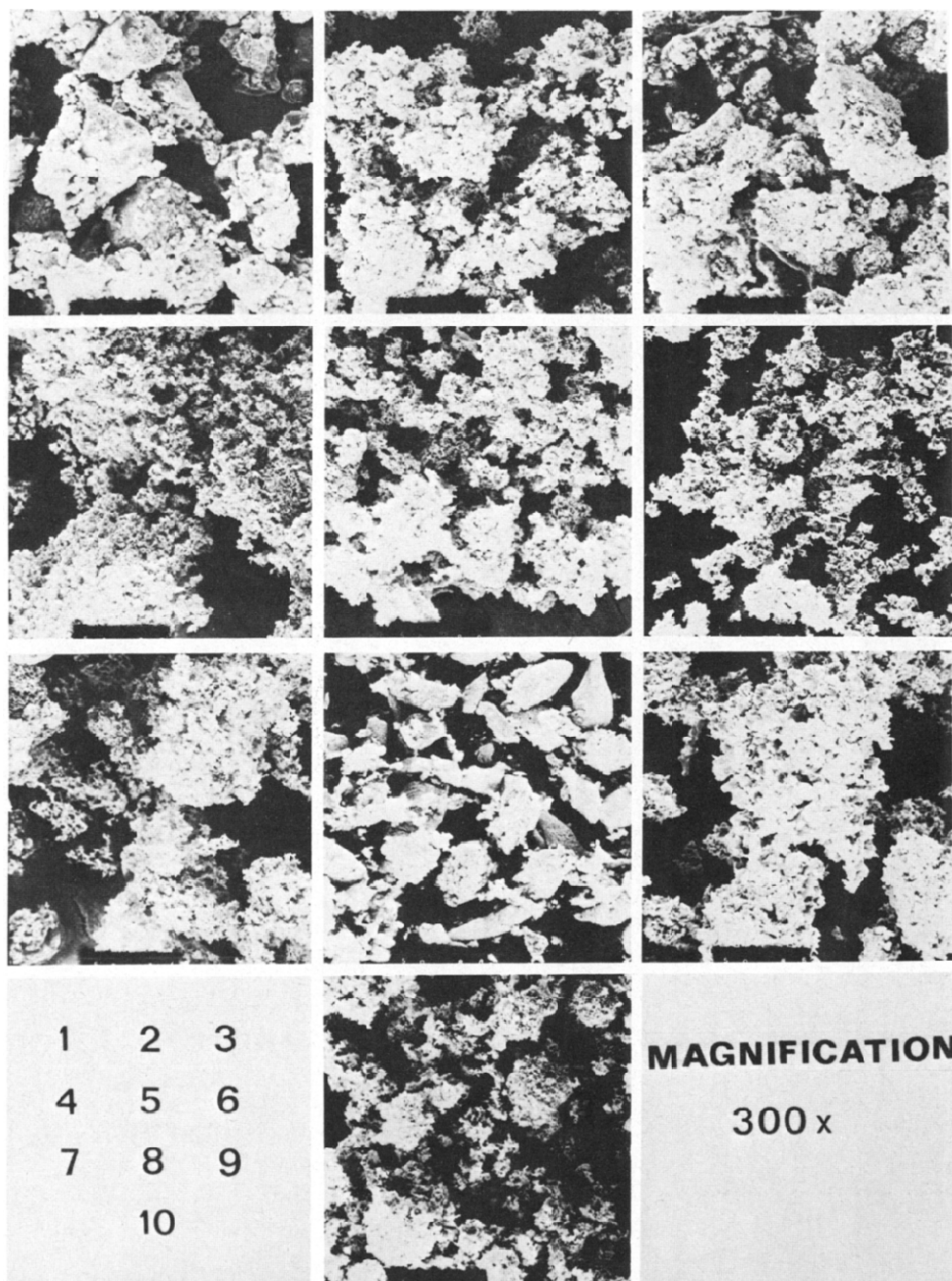
Fig. 3. Microphotographs of the catalysts by scanning electron microscope. (The identification of the catalysts is identical with Table 1.)

The last method for the catalysts evaluation was the decomposition of hydrogen peroxide solution by Ag powder (200 ml N H_2O_2 in 7 N KOH,
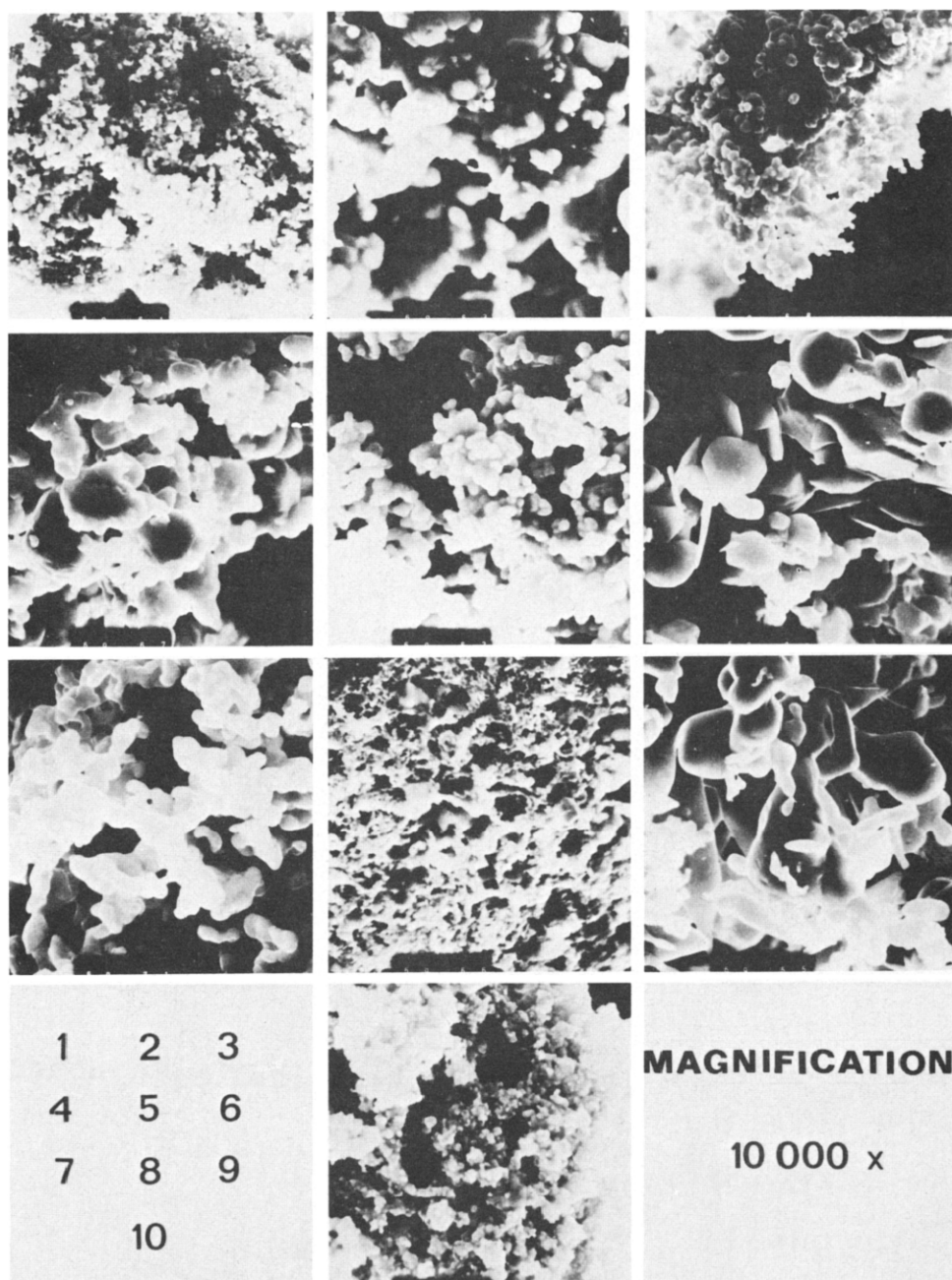
Fig. 3(b). (*For legend please see preceding page.*)

293 K; 0.1 g Ag). The process of decomposition was followed by measurement of the volume of gas evolved and the results for some catalysts are given in Fig. 4. The evaluation of the whole set is given in Table 3 according to the slope of the straight line part of the time–volume ($\Sigma V/t$) curves.
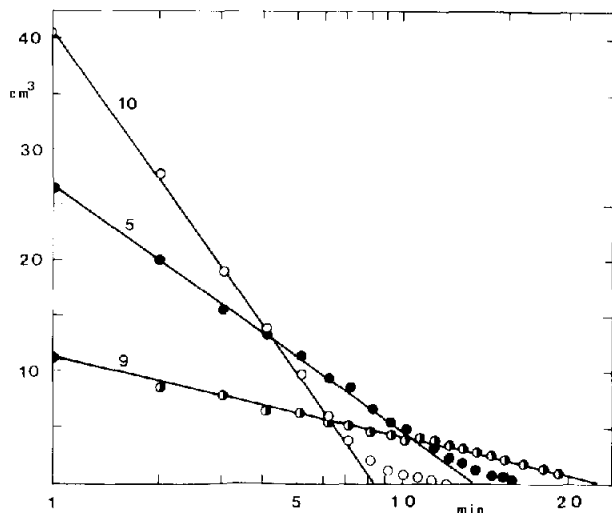
Fig. 4. Volume of oxygen evolved during the decomposition of H_2O_2 in alkaline solution. (The identification of the catalysts is identical with Table 1.)

The mutual comparison of the applied methods is expressed by the sequences of catalysts in Table 3. An absolute agreement was obtained for the first and the last members of the investigated catalysts when comparing the specific surfaces, the RTG analysis and scanning observations. The deviation of the middle members of this set is easy to understand from the relatively small differences between the individual values. It can be said that the three physical methods which are closely related provided results within reasonable agreement.

The evaluation of the catalysts by means of hydrogen peroxide decomposition proved to be quite different and the results were not in direct correlation with the size and surface articulation because the catalyst active centres took part in the decomposition. Hence the sequence of catalysts in the set according to this method was different.

Considering the electrochemical activity as the last and decisive criterion, catalyst 9 was explicitly determined by all the applied methods as the worst one. As far as the remaining catalysts are concerned the physical methods applied for the determination of catalyst surface and the structure of the grains cannot be used to evaluate the electrochemical activity. From this point of view catalyst 3 is interesting. Despite some good physical parameters its electrochemical activity was low: its surface is covered by a sulfide layer formed during preparation.

Also the heterogeneous catalytic decomposition of the hydrogen peroxide proved not to be an unequivocal criterion for the evaluation of small differences in the electrochemical activity of Ag catalysts. This process can distinguish the catalysts with considerable differences in electrochemical characteristics (e.g. catalysts 9 and 10) but it cannot find out differences among the others catalysts.

Finally, it can be said that the only safe way to evaluate electrochemical catalyst activity was verification in the real electrode. Our experimental results showed that not all the active catalysts tested in the form of a fine powder are suitable for the preparation of satisfactory hydrophobic air electrodes. The different mechanism of oxygen transport to an active interface in the semihydrophobic operating layer requires a catalyst which makes possible a uniform distribution of the fine catalyst particles in the PTFE substance. The silver catalyst arising in the form of fine well disintegrated particles is especially suitable for this purpose (catalysts 7, 8, 10). Catalysts having a complicated internal structure and very articulated shapes do not utilize these properties in the hydrophobic electrode because of flooding of the small capillaries so that only the external surface is functioning. Gas without an overpressure does not expel the liquid from the internal pores in the grains.

The high electroactivity of catalyst 10 has not been explicitly explained. Probably this fine silver powder has changes in its structure and surface oxide layer that were caused by admixtures entering into the catalysts during its preparation.

Comparison of the hydrophobic and hydrophilic electrodes

The hydrophilic electrodes prepared by sintering were annealed at a temperature of 723 K which could cause the catalyst surface to be diminished owing to recrystallization. Comparison of the activities of the three types of electrodes (hydrophilic sintered electrodes, hydrophilic unsintered electrodes and hydrophobic air-breathing unsintered electrodes) prepared from the same catalyst could lead to the elucidation and verification of changes occurring during the sintering. The active layer of the sintered electrodes contained a mixture of the catalyst and carbonyl nickel in the ratio 1:2. The active layer of the others electrodes contained the catalyst only with a small amount of PTFE bonding agent. The amount of the catalyst on unit surface is given in Table 4. The sintered electrodes had the larger amount of the silver catalyst which resulted from the greater thickness of the applied operating layer. It is seen in Fig. 5 that the reduction of the operating layer thickness to the catalyst load of 80 mg Ag/cm^2 may be achieved essentially without change in the electrode potentials. The potential data E in Table 4 can therefore be considered as mutually comparable.

Catalyst 9 was not very active and proved to be unsuitable for sintered electrodes as may be seen from the results presented for the electrodes in Table 4. The catalytic silver 10 was again confirmed as the most suitable. The silver prepared by oxalate decomposition or by leaching a silver alloy also provided very good activity.

The relatively small differences in the measured potentials of these three types of electrodes operating with the same silver catalyst showed that the sintering did insufficient damage to the catalyst to cause the electrochemical activity of the electrodes to vary significantly. Sintering changes the catalyst surface only within limits having no great influence on its catalytic activity. The supporting skeleton structure of the carbonyl nickel in the sintered elec-

trodes prevents silver particles from mutual contact and also therefore their recrystallization. Moreover the original little developed surface is not changed or damaged.

TABLE 4

Electrochemical activity of different oxygen electrodes. Potential E_i (V) at the current density $i = 0.1$ A/cm^2. Catalyst load M in mg/cm^2. Temperature 373 K, gas overpressure 0.07 MPa.

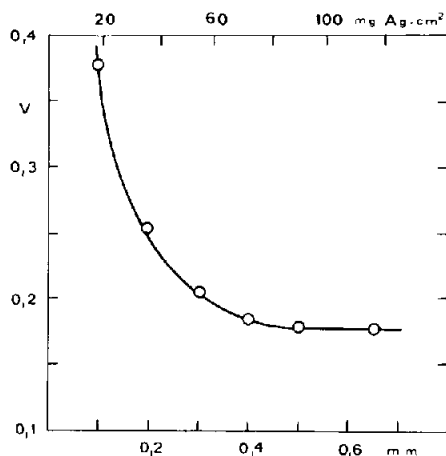| Kind of electrode	Catalyst No.							
	7		8		9		10	
	$-E_i$	M	E_i	M	E_i	M	E_i	M
Hydrophilic sintered, gas overpressure	0.075	117	0.120	123	0.180	120	0.063	125
Hydrophilic unsintered, gas overpressure	0.110	85	0.085	96	0.336	92	0.035	87
Hydrophobic unsintered	0.060	69	0.287	77	0.410	84	0.020	60

Fig. 5. The potential dependence of the sintered oxygen electrode (operating with gas over pressure) on the thickness of the operating layer and the catalyst load (using catalyst 8).

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