

Influence of pretreatment of active carbon on the properties of porous carbon electrodes for preparing hydrogen peroxide by cathodic reduction of oxygen

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Preparation of hydrogen peroxide by cathodic reduction of oxygen in porous electrodes from active carbons without or with a thermal pretreatment at min. 1000°C either *in vacuo* or in the presence of alkali sulfides in an inert atmosphere at normal pressure was investigated. The current yields of hydrogen peroxide on electrodes from untreated active carbons are initially very low and rise slowly with time up to ca. 15—25%. The thermal pretreatment of active carbon *in vacuo* results in a pronounced increase of current yields up to 60—80% (at 30 mA cm⁻²); from this value they begin to decrease and after several hours they reach the level equal to that for untreated carbon. The most effective treatment consists in heating active carbon in an inert atmosphere with alkali metal sulfides; for this treatment the optimum temperature and time of heating were found. The lifetime of such electrodes reaches in best cases about one thousand hours. A continual feeding of the inlet electrolyte with catalytic poisons (HgO, As₂O₃) has no effect on current yields of hydrogen peroxide when using electrodes from untreated active carbon.

Было исследовано получение перекиси водорода катодическим восстановлением кислорода в пористых электродах из активного угля добавочно обжиганного при температуре мин. 1000°C или в вакууме или в присутствии сернистого натрия или калия при нормальном давлении инертного газа. Выходы по току перекиси водорода на электродах из не обработанного угля сначала очень низкие и возрастают медленно до 15—25%. Термическая обработка активного угля в вакууме вызывает резкое повышение выходов по току (до 60—80% при плотности тока 30 мА см⁻²), но это действие только краткосрочное и выходы по току опять постепенно падают до уровня для не обработанного угля. Наиболее эффективным является обжиг активного угля с сернистым натрием или калием в атмосфере азота или другого инертного газа, и для такой обработки были установлены оптимальные условия. Срок службы электродов из таких углей достигал около тысячи часов. Непрерывное отравление пористых угольных электродов каталитическими ядохимикатами HgO и As₂O₃ из протекающего электролита не влияет на выходы по току перекиси водорода при использовании электродов из не обработанного угля.

In our previous paper [1] we have dealt with the electrochemical preparation of hydrogen peroxide by the cathodic reduction of oxygen in solutions of sodium or potassium hydroxides using porous cathodes prepared from various commercial sorts of active carbon or powdered graphite, according to patent specification [2]. The results showed that the current yields of hydrogen peroxide at current densities

5—50 mA cm⁻² on electrodes prepared from untreated carbonaceous materials reached in short time experiments only 0—30%, which is too low for a technical application. In the same paper also some results of experiments with porous electrodes prepared from active carbon pretreated by heating with sodium or potassium sulfides in nitrogen atmosphere [3] were reported. The results unambiguously proved a pronounced increase of current yields of hydrogen peroxide to such a level which is technically very promising. The increase of current yields of hydrogen peroxide can probably be explained by poisoning the active centres of active carbon for hydrogen peroxide decomposition by sulfur compounds.

In this communication the results of experiments with poisoning porous electrodes from untreated active carbons by catalytic poisons (As, Hg) added directly into the flow of inlet electrolyte, further of experiments with thermal pretreatment of active carbon by heating *in vacuo* according to *Kastening* and *Faul* [4, 5], and finally of the experimental determination of the most suitable procedure for the pretreatment of active carbon with alkali metal sulfides in an inert atmosphere [3] are presented.

Experimental

The influence of various treatments of active carbons on their suitability as starting material for the preparation of porous electrodes for the production of hydrogen peroxide by cathodic reduction of oxygen was examined in a laboratory scale flow electrolyzer described in [1]. The porous electrodes were prepared from powdered carbonaceous materials in the same way.

As catalytic poisons added directly into the inlet solution of sodium or potassium hydroxide, As₂O₃ and HgO were used. The former dissolved very well in the solution under the formation of AsO₂⁻, the solubility of the latter in the used electrolytes was very low. It was assumed that the concentration of poisoning agents does not change during the stay of electrolyte in the anodic compartment, though the ions AsO₂⁻ are probably oxidized to AsO₃⁻. After passing through the percolating diaphragm into the cathodic compartment the AsO₃⁻ ions are reduced back to As(III).

The pretreatment of active carbon according to *Kastening* and *Faul* [4, 5] consisted in heating active carbon Desorex and Carboraffin at ca. 1000°C for 30 min at a reduced pressure (approximately 1 kPa). The pretreatment of active carbon by heating with sodium or potassium sulfide [3] consisted in preparing a homogenized slurry of active carbon with a saturated or diluted solution of alkali metal sulfide of technical purity, its drying and heating in nitrogen at 1100—1300°C (1 1/2—2 1/2 h). After cooling in nitrogen, the treated carbon was washed with boiling hydrochloric acid and then thoroughly rinsed first with boiling and finally with cold distilled water and dried.

Further, the influence of different reaction conditions during the heating of active carbon with sulfides on the rate of spontaneous decomposition of hydrogen peroxide solution in 5 N-KOH was examined by measuring the rate of evolution of gaseous oxygen from a mixture of 20 cm³ 5 N-KOH and 1 cm³ 80% H₂O₂ with 0.1 g of active carbon sample. The reaction vessel as well as the gas burette were kept at 20°C.

Results and discussion

The results of experiments with porous cathodes from untreated active carbon poisoned by catalytic poisons added into the inlet electrolyte are given in Table 1. Low solubility of HgO in the used electrolyte required a very long time of electrolysis in order to supply sufficient amount of poison to the porous electrode. In order to obtain comparable results it was necessary to carry out experiments with pure electrolyte under similar conditions.

From Table 1 it follows that the current yields of hydrogen peroxide in the absence of poison were almost zero on electrodes from Carboraffin at the beginning of the experiment, and they slightly increased if the electrode was working for a sufficiently long time, especially at low current densities. Electrodes from Desorex produced hydrogen peroxide with current yields 12–20% at a current density 33 mA cm^{-2} in 5 N-KOH as well as in 2 N-NaOH at 20°C . Very similar results were obtained with electrodes from untreated active carbon Super-sorbon (ČSSR) and from active carbon of Degussa (GFR) (not given in Table 1).

The results of experiments with catalytic poisons HgO and As_2O_3 added directly into the inlet electrolyte showed practically no influence on the current yields of hydrogen peroxide. Even the impregnation of porous electrode with a concentrated solution of HgCl_2 in ethyl alcohol (50.5 g HgCl_2 in 100 g $\text{C}_2\text{H}_5\text{OH}$ at 25°C) before drying the electrode did not practically increase the current yields of hydrogen peroxide.

The results of experiments with two samples of active carbon treated according to *Kastening* and *Faul* [4, 5] are given in Table 2. It is evident that such a procedure causes a marked increase of current yields of hydrogen peroxide, but its promoting action is — at least for the sorts of active carbon used in our experiments — sufficiently effective for a limited time only. At a current density 33 mA cm^{-2} the current yields decreased after ca. 50 h to values corresponding to electrodes from untreated active carbons. At lower current densities, the effect of this procedure was somewhat prolonged but even in this case it was rather ineffective for practical applications.

In experiments with the pretreatment of active carbon by heating with sodium or potassium sulfide only Carboraffin was used, because it gave the lowest current yields of hydrogen peroxide in the untreated state. The aim of these experiments was mainly to find the optimum duration and temperature of heating of the dried mixture of active carbon with sodium or potassium sulfide in nitrogen (Table 3).

From the experimental results it follows that for each temperature there is an optimum time of heating after which the current yields of hydrogen peroxide decrease abruptly (Fig. 1). Temperature 1200°C and the time of 2 1/4 h were found to be the most convenient. Similar results were obtained when heating a dried mixture prepared from active carbon and rather diluted solutions of

Table 1

Influence of addition of catalytic poisons HgO and As₂O₃ into the inlet electrolyte on current yields of hydrogen peroxide by cathodic reduction of oxygen in porous carbon electrodes

Active carbon	Electrolyte	Poison	<i>t</i> h	mA cm	Voltage V	Current yields
Carboraffin	2 N-NaOH	—	23	33	1.85	0
		—	114	33	1.85	0.25
		—	160	16.5	1.42	2.5
		HgO	200	16.5	1.42	2.5
		HgCl ₂	225	16.5	1.42	2.6
		(impreg.)				
		HgCl ₂	240	6.6	1.18	19.5
		HgCl ₂	432	6.6	1.18	14.5
		HgCl ₂	440	3.3	1.10	20.0
		HgCl ₂	562	3.3	1.00	20.5
Desorex	5 N-KOH	—	48	33	1.0	12.8
		—	220	33	1.0	18
		—	363	33	1.0	12
	2 N-NaOH	—	400	33	1.1	13
		—	450	33	1.1	20.8
		—	522	33	1.1	15.5
		HgO	536	33	1.1	16
		HgO	684	33	1.1	19
		HgO	860	33	1.1	19
		HgCl ₂	990	33	1.1	23.5
		(impreg.)				
Desorex (another electrode)	2 N-NaOH	—	24	33	1.4	20.5
		—	70	33	1.4	20.0
		—	190	16.5	1.22	17
		—	281	16.5	1.22	33
		—	333	6.6	0.85	23
		—	370	6.6	0.85	30
		—	440	3.3	0.75	18
		—	584	3.3	0.75	22
	5 N-KOH	—	42	33	1.1	17
		As ₂ O ₃ ^a	175	33	1.1	16
		As ₂ O ₃ ^a	320	33	1.1	18
		As ₂ O ₃ ^a	426	33	1.1	21
		As ₂ O ₃ ^a	439	33	1.1	19.5
		—	661	33	1.1	8

a) 6.25 g As₂O₃/l; b) 12.5 g As₂O₃/l.

Table 2

Influence of the thermal treatment of active carbon *in vacuo* on current yields of hydrogen peroxide by cathodic reduction of oxygen in 2 N-NaOH at 20°C

Active carbon	Conditions of heating	Time of electrolysis h	i_c mA cm^{-2}	Voltage V	Current yields %
Desorex	1000°C 30 min	15	33	1.40	78
		58	33	1.50	12
		79	33	1.52	9
		106	16.5	1.30	9
Carboraffin	1250°C 30 min	8	33	1.35	12
		40	33	1.48	9
		103	33	1.62	5
		147	6.6	1.36	24
		170	6.6	1.37	24
		197	6.6	1.45	23

potassium sulfide. For example, an electrode prepared from active carbon mixed before heating with a solution of 0.9 M- K_2S produced hydrogen peroxide during 100 h at a current density 33 mA cm^{-2} with current yields of 78%, then the current yields decreased slowly to 65% after 218 h when the experiment was interrupted. An electrode prepared from a mixture of active carbon with a solution of 1.8 M- K_2S before heating produced after 165 h of operation at the same conditions

Table 3

Influence of different conditions of the thermal treatment of active carbon Carboraffin with sodium sulfide on current yields of hydrogen peroxide by cathodic reduction of oxygen in porous electrodes made of pretreated carbons in 2 N-NaOH at flow rate $30 \text{ cm}^3 \text{ h}^{-1}$ at 20°C

Temperature of heating °C	Time of heating h	Current yields (%) at current density i_c , mA cm^{-2}			
		8.3	16.5	25	33
1100	2.0	—	77	69	50
1150	2.0	—	85	79	70
1200	1.5	68	55	32	28
	2.0	84	86	83	77
	2.5	88	86	84	69
1250	1.5	86	83	75	65
	2.0	78	76	70	59
	2.5	78	75	70	59
1300	2.5	56	—	—	29

of electrolysis hydrogen peroxide with current yields of 76.2% in comparison to 78% at the beginning of the experiment. The lifetime of electrodes prepared from a heated mixture of active carbon with a practically saturated solution of potassium sulfide (ca. 7 M) reached for optimum heating conditions approximately one thousand hours without any marked decrease of current yields of hydrogen peroxide.

The data on the influence of the thermal treatment of active carbon with sulfides on the initial rate of spontaneous decomposition of hydrogen peroxide in alkaline solutions are given in Table 4.

Table 4

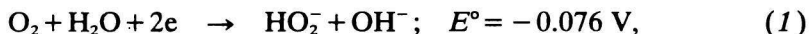
Rate of decomposition of hydrogen peroxide solution in 5 N-KOH
by active carbon Carboraffin heated with sodium sulfide
at different temperatures

Temperature of heating °C	Time of heating h	Surface area m ² g ⁻¹	Rate of oxygen evolution cm ³ min ⁻¹ g ⁻¹ cat. c
1100	2.0	—	27
1200	2.5	1100	8.2
1250	2.0	—	12
1300	2.5	165	13.2
non heated	—	1100	22.2

From a comparison of these data with those of Table 3 it is evident that the treatment of active carbon leading to the highest current yields of hydrogen peroxide results also in the lowest catalytic activity with respect to the spontaneous decomposition of hydrogen peroxide. Contrary to that active carbons heated with sulfide at conditions differing from the optimum ones accelerate the hydrogen peroxide decomposition several times. Very interesting is also the observation that the specific surface area of active carbon (measured by the BET method) remains unchanged during heating at 1200°C whereas heating at 1300°C diminishes this quantity approx. by an order. In spite of this fact active carbon heated at 1300°C accelerates the decomposition of hydrogen peroxide several times if compared with active carbon heated at optimum conditions for maximum current yields of hydrogen peroxide.

The positive influence of heating of active carbon with sodium or potassium sulfide on the current yields of hydrogen peroxide by cathodic reduction of oxygen may be explained in the following manner.

Oxygen may be reduced in alkaline medium in two different ways. The first one consists in a two-electron process under the formation of perhydroxyl anion



which may further be reduced in the subsequent step to hydroxyl ion



The second one is expressed by an overall four-electron reduction directly to hydroxyl ions



The rate of the individual electrode processes depends mainly on the nature of electrode material. It was found that on electrographite, glassy carbon, and active carbon, the reduction of oxygen proceeds *via* hydrogen peroxide (eqns (1) and (2)) [6, 7]. Further it was found that on active carbon the rate of reaction (1) is of the same order as on pyrographite, but the rate of hydrogen peroxide reduction (eqn (2)) on active carbon is higher [8]. The high activity of untreated active carbon with respect to the acceleration of hydrogen peroxide decomposition is attributed to a high concentration of oxygen-containing compounds on the surface of carbon [9]. We also assume that the catalytic activity of active carbon in the hydrogen peroxide decomposition may be caused by a high concentration of unpaired electrons (they are the paramagnetic centres) the presence of which on

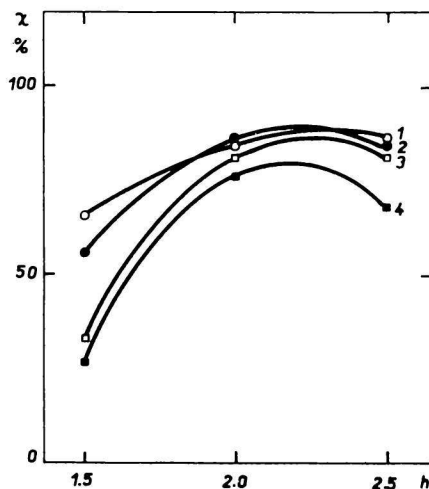


Fig. 1. Influence of duration of the heating of active carbon with sodium sulfide at 1200°C on current yields of hydrogen peroxide on porous electrodes made from thus treated carbons at various current densities in 2 N-NaOH at flow rate 30 cm³ h⁻¹ at 20°C.

Cathodic current density: 1. 8.3; 2. 16.5; 3. 25; 4. 33 mA cm⁻².

the surface of active carbon is connected with oxygen-containing radicals [10]. The untreated active carbon accelerates therefore not only the overall hydrogen peroxide reduction according to reaction (2), but also its spontaneous decomposition according to the overall reaction



Heating of active carbon with alkali metal sulfides causes the formation of very stable C—S groups on its surface [11]. *Siedlewski* found by means of e.p.r. measurements [12, 13] that the irreversibly adsorbed hydrogen sulfide did not decrease the concentration of unpaired electrons on the surface of active carbon, but it prevented their interaction with molecular oxygen. Analogously it may be assumed that the surface C—S groups formed upon heating with sulfides inhibit the surface oxygen-containing radicals to interact with oxygen from hydrogen peroxide, and in such a way they retard its reduction according to eqn (2), as well as its spontaneous decomposition according to eqn (4). This assumption was confirmed experimentally. Therefore, on electrodes from active carbons with strongly bound sulfur on their surface the formation of hydrogen peroxide according to eqn (1) proceeds with markedly higher current yields than on electrodes prepared from untreated active carbons.

An elementary analysis of two samples of active carbon heated with sulfides (Table 5) showed that the total content of sulfur increased by several per cent. Simultaneously it was found that porous electrodes prepared from active carbon with the highest content of sulfur (9.5% S) produced hydrogen peroxide with the highest current yields.

Further it was found that from the total amount of sulfur in this case (9.5% S) there were 5.8% extracted into CS₂, probably in the form of elementary sulfur. This gives a clear evidence of a very strong bond between sulfur and the surface of active carbon which is maintained even at 1200°C. The results presented in Table 5 show further that an increase in sulfur content caused a decrease in the hydrogen content, whereas the content of oxygen (calculated as the rest to 100%) was affected only a little by heating with sulfides. This is in a good agreement with the finding of *Siedlewski* [12, 13] about the influence of hydrogen sulfide adsorption on the concentration of oxygen-containing radicals with unpaired electrons on the surface of active carbon.

On the basis of presented interpretation it is also possible to explain the observed short time effect of the heating of active carbon *in vacuo* according to *Kastening* and *Faul* [4, 5] on the current yields of hydrogen peroxide. From the literary data it is known that heating of microcrystalline carbon at temperatures higher than 600°C in an inert atmosphere or *in vacuo* causes a progressive removal of oxygen bonded on the surface [14] which is practically completed at 1200°C, and thus also

Table 5

Elementary analysis of active carbon Carboraffin untreated
and after heating with Na_2S under different reaction conditions

Temperature of heating °C	Time of heating h	Elementary analysis in mass %				
		C	H	S	N	O (as rest to 100%)
non heated	—	83.95	2.62	0.24	0.25	12.94
1100	2	83.36	0.90	4.08	0.08	11.58
1200	2	78.60	0.69	9.50	0.39	11.02

a decrease of concentration of unpaired electrons [15]. The increase of current yields of hydrogen peroxide with porous electrodes from thus treated active carbon at the beginning of electrolysis is most probably caused by a thermal removal of surface oxygen groups acting as catalytic centres for hydrogen peroxide decomposition. However, such a surface seems to be not stabilized and not inhibited against the subsequent action of oxygen and/or hydrogen peroxide. As it is in contact with these species during the electrolytic reduction of oxygen, it may be reoxidized under the formation of surface oxygen groups with described catalytic properties. Therefore, the current yields of hydrogen peroxide are high enough only for a limited time, when the surface of porous carbon electrodes is sufficiently free of such oxygen-containing groups. During an extended processing in a continually working flow electrolyzer, their amount rises successively. Consequently, the current yields of hydrogen peroxide decrease (in our cases in 2—5 days) to the values practically concurrent with those obtained with electrodes from untreated active carbon.

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