

RELATION BETWEEN THE ACTIVITY OF ELECTRODES FROM VARIOUS CARBONACEOUS MATERIALS FOR REDUCTION OF OXYGEN TO HYDROGEN PEROXIDE AND CONCENTRATION OF THEIR PARAMAGNETIC CENTERS

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The current yield of hydrogen peroxide during cathodic reduction of oxygen in porous electrodes from various carbonaceous materials is the lower the higher is the number of paramagnetic centers in these materials. A substantial decrease in the concentration of paramagnetic centers by heating to 900°C in vacuum is only temporary, whereas by heating with alkali metal sulphides it is practically permanent.

We found¹ that low current yields of hydrogen peroxide during oxygen reduction in alkaline medium on porous electrodes made of untreated active carbons can be markedly increased by pre-heating the active carbons with alkali metal sulphides in an inert or hydrogen atmosphere² at 1000–1300°C. According to Kastening and Faul^{3,4}, a similar effect can be achieved by heating the active carbons at 900°C in vacuum. However, application of this method to our active carbon samples had only a transitional effect¹ lasting for several tens of hours whereas the thermal treatment with sulphide is much more durable (of the order of 10³ h), as judged on the basis of the current yield. High current yields of hydrogen peroxide can be attained also on porous electrodes made of certain sorts of untreated carbon black^{5–7}. Differences in the current yields were attributed to different activity of the carbonaceous materials with respect to spontaneous decomposition of alkaline hydrogen peroxide solutions, which was proved experimentally^{1,6}, and elucidated on the basis of different concentrations of surface oxygen radicals with unpaired electrons^{8–10}. It is also known that the concentration of paramagnetic centers in carbonaceous materials increases by oxidation (*e.g.*, with O₃ or HNO₃)^{11,12} and decreases by heating in vacuum¹³.

We therefore decided to measure the concentration of paramagnetic centers in the carbonaceous materials used in preparation of porous electrodes for reduction of oxygen to hydrogen peroxide^{1,6}, and thus to obtain an evidence for its significance for the given electrode process.

EXPERIMENTAL

Carbonaceous materials. The concentration of paramagnetic centers was measured on untreated active carbon of the type Carboraffin and Desorex, further on Carboraffin heated with K₂S at 1200°C for 2 h, on both active carbons heated in vacuum for 30 min at 1000°C, and

on carbon black of the type PM 16 E. The sample heated with K_2S was prior to measurement stored in a glass bottle in the presence of air for 57 months, the samples heated in vacuum were thus stored for 25 months. Besides, other samples heated in vacuum were used for the measurement of EPR spectra three days after their preparation. The characteristics of these materials with regard to their use in electrodes for the reduction of oxygen according to our measurements^{1,6} are given in Table I.

Measurement of EPR spectra was carried out on a JEOL JES-3B type apparatus in the X band at room temperature and modulation 100 kHz. Calibration was carried out with Mn^{2+} , diphenylpicrylhydrazyl and a carbon standard.

RESULTS AND DISCUSSION

Evaluation of the EPR spectra of the studied samples is given in Table II. It is seen that the concentration of paramagnetic centers in untreated Carboraffin ($95 \cdot 10^{17} g^{-1}$) decreases by two orders of magnitude by heating in vacuum at $1000^\circ C$, it is however practically restored after prolonged storage in contact with air at room temperature (25 months), attaining $79 \cdot 10^{17} g^{-1}$. In the case of Carboraffin heated with K_2S , no EPR signal was obtained even after 57 months of storage, an evidence that the concentration of paramagnetic centers was effectively and durably suppressed below

TABLE I

Dependence of Current Yield of Oxygen Reduction to H_2O_2 on Time of Electrolysis with Porous Electrodes from Various Materials

Current density $j_c = 0.033 A/cm^2$; $20^\circ C$.

Material	Time of el., h	Current yield, %
Carboraffin untreated	8	0.3
	48	0.28
	114	0.25
Carboraffin heated in vacuum	8	12
	103	5
Carboraffin heated with K_2S	15	78
	165	76.2
	1 006	74
Desorex untreated	48	12.8
	363	12
Desorex heated in vacuum	15	78
	58	12
Carbon black PM 16 E	21	94
	288	95

the detection limit of the method. In contrast, with active carbon Desorex either untreated or heated in vacuum, only a small signal was obtained under the same conditions of measurement, the concentration of paramagnetic centers being by two orders of magnitude smaller than with the untreated Carboraffin. In the case of the carbon black PM 16 E, which was not specially treated, no marked EPR signal was obtained similarly to active carbon Desorex and Carboraffin heated with K_2S .

Comparing the results in Table I with the data in Table II it is seen that the current yield of peroxide is the higher the lower is the concentration of paramagnetic centers on the surface of the carbon used in the porous electrode. Heating of Carboraffin with K_2S causes elimination of the EPR signal and a marked increase of the current yield of peroxide from almost zero to about 75% (ref.^{1,2}). Sole heating in vacuum³ depresses the EPR signal incompletely and for a limited time, so that the current yield after 100 h decreases from the initial 12% to 5% and further on. In accord with this, the vacuum-heated sample gave after 25 months of storage practically the same EPR signal as the untreated one. It follows that heating at 1000°C in vacuum decreases the concentration of paramagnetic centers on the active carbon surface only temporarily and these centers can be restored after prolonged contact with an oxidant (air, H_2O_2) to catalyse the decomposition of hydrogen peroxide and thus diminish its current yield during electroreduction of oxygen. It is probable that the concentration of paramagnetic centers increases in the porous electrode during electroreduction of oxygen more rapidly than in contact with air, since the electrode is subjected to a relatively high concentration of peroxide, which is formed in their pores. An increase in the concentration of paramagnetic centers was observed also in the case of carbon prepared by pyrolysis of cane sugar at 1000°C after contact with oxygen at room temperature¹⁴.

TABLE II
Concentration of Paramagnetic Centers in 1 g of Carbonaceous Material

Material	$c \cdot 10^{-17} \text{ g}^{-1}$
Carboraffin untreated	95
Carboraffin heated in vacuum	0.77
Preceding one stored 25 months open to the air	79
Carboraffin heated with K_2S	0 ^a
Desorex untreated	1.1
Desorex heated in vacuum	0.59
Carbon black PM 16 E	2.5

^a Concentration below the sensitivity limit of the method.

Heating in vacuum increased the current yield of peroxide also with electrodes from active carbon Desorex, whose surface concentration of paramagnetic centers is in the untreated state by about two orders of magnitude lower than with the untreated Carboraffin. In this way, the initial current yields were increased up to values corresponding to this material treated with K_2S . Sole heating in vacuum had also in this case only a temporary effect, since already after 60 h of electrolysis the current yield dropped to a level corresponding to the untreated sample of this carbon. The more durable effect of heating the active carbon with K_2S can be on the basis of EPR measurements interpreted so that this procedure removes the paramagnetic centers responsible for the catalytic effect of the untreated carbon samples on the peroxide decomposition as a result of the formation of very stable C—S bonds¹⁵, which do not split even after a 57-month stay in the air atmosphere. It is hence conceivable that the current yields on electrodes from such a carbon did not drop under 70% even after more than 1000 h of operation under the given conditions. The elimination of paramagnetic centers on the surface of active carbon heated with alkali metal sulphides is in contrast with the results of Siedleski¹⁶ about adsorption of H_2S on active carbon at 20°C, according to which the concentration of paramagnetic centers does not change, but the catalytic activity of this carbon toward oxidation reactions decreases. It is hence apparent that the effect of sulphides on active carbon at higher temperatures is much more profound than the effect of H_2S at normal temperature. The nature of chemical changes of surface groups by heating with sulphides was not examined. It is interesting to note that the content of oxygen in the carbon is according to elementary analysis practically uninfluenced by heating with the alkali metal sulphide¹.

Our results show doubtless an indirect dependence between the surface concentration of paramagnetic centers and current yield of cathodic reduction of oxygen to hydrogen peroxide on porous carbon electrodes. A quantitative relation, however, cannot be found since the surface concentration of paramagnetic centers on the carbon may undergo changes during electrolysis according to the nature of the carbon and its pretreatment. The current yield of H_2O_2 can be influenced also by the specific surface area of the carbon electrode, which can catalyse the decomposition of the peroxide^{17,18}. The use of active carbon with a low concentration of paramagnetic centers as electrode material is preferable especially when its specific surface area is relatively low. Thus, the differences between the current yields with electrodes from carbon black PM 16 E and active carbon Desorex can be understood, the specific surface area of the latter being about 50 times that of the black although the concentration of paramagnetic centers being of the same order in both cases.

Consequently, the EPR measurement can serve as a rapid and reliable qualitative test to judge the suitability of a given sort of carbon for the preparation of porous electrodes for reduction of oxygen to hydrogen peroxide, before a long-term experiment be made.

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