

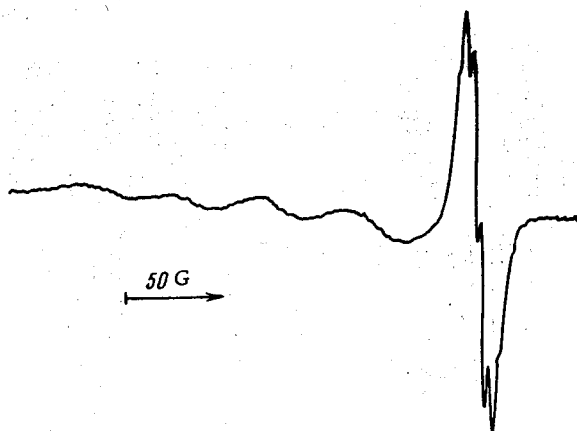


Fig. 2. The EPR spectrum recorded during the first minute after the start of the reaction between copper(II) chloride and N-dimethylaniline in acetone. $T = 295^\circ\text{K}$; reagent concn.: CuCl_2 0.02 M, amine 0.5 M.

fifth minute after the start of reaction, the hyperfine structure of the EPR spectrum of the radical cation clears up and acquires the form shown in Fig. 1a.

The kinetic investigations showed that the radical cations we discovered are stable over a period of several hours.

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ELECTROCATALYSIS OF OXYGEN REDUCTION AT METAL CHELATES IN ACIDIC ELECTROLYTES

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UDC 541.133.08

The development of an oxygen (air) cathode for acidic media which does not contain scarce metals is an important current problem in the area of electrochemical power sources. With the solution of this problem one will be able to escape the difficulties associated with carbonate formation in alkaline electrolytes when organic fuels or contaminated hydrogen and air oxygen as the oxidizing agents are used. Carbon-based oxygen electrodes for acidic media promoted by organic metal complexes (phthalocyanines, tetraarylporphins) are described in [1-4]. Carbon black [1] or activated carbons [2-4] were used as supports. The catalyst was introduced into the support by soaking the carbon with a solution of the organic complex in concentrated sulfuric acid or in a suitable organic solvent. Hydrophobized

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. (Presented by Academician S. I. Vol'fkovich November 5, 1976.) Translated from Doklady Akademii Nauk SSSR, Vol. 233, No. 5, pp. 889-891, April, 1977. Original article submitted October 26, 1976.

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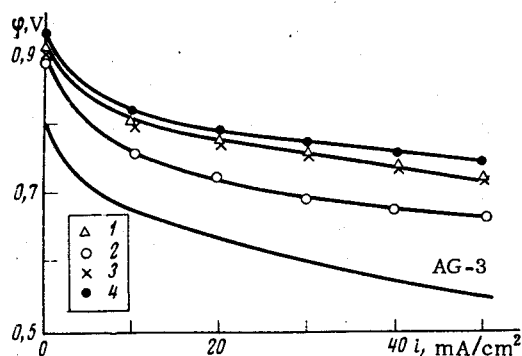


Fig. 1. Electrochemical characteristics of porous carbon electrodes promoted with organic cobalt complexes, in 4.5 N H_2SO_4 at 20°C: 1) CoTMPP without heat treatment; 2, 3, and 4) heat-treated CoTBP, CoTPP, and CoTMPP, respectively; the solid curve: AG-3 without catalyst.

electrodes were used where a stable interface between gas and electrolyte was set up by adding a hydrophobizing agent (fluoroplast [polytetrafluoroethylene], polyethylene) which simultaneously functioned as the binder.

According to the data of [1], the potential of a carbon electrode promoted with iron phthalocyanine polymer (FePc_1) is 0.85 V at a current density of 10 mA/cm^2 (the potentials are reported relative to a hydrogen reference electrode in the same solution). However, the electrodes are unstable. Electrodes activated with cobalt phthalocyanine polymer (CoPc_1) retain their activity over a period of about 150 h, but then also show decreasing performance. The instability of the electrochemical properties of carbon-based oxygen electrodes containing phthalocyanines which is found in acidic solutions probably is due to partial dissociation of the tetrabenzotetraazaporphin complexes [4, 5]. Negative effects can also be exerted by hydrogen peroxide which is produced in acidic solutions as an intermediate of oxygen reduction and which can oxidize metal phthalocyanines with cleavage of the macroring [5]. The oxidizability decreases when one goes to the tetrabenzoporphin complexes. Electrodes consisting of Norite active carbon, 5 wt. % of cobalt tetra(p-methoxyphenyl)porphin (CoTMPP) and binder showed stable operation over a period of 300 h in 3 N H_2SO_4 , according to the data of [4].

We have developed a method of activating carbon electrodes with organic cobalt complexes (CoPc, Co tetraphenylporphin CoTPP, CoTMPP, and Co tetrabenzoporphin CoTBP) which yields long-term stable performance of the oxygen electrodes in 4.5 N H_2SO_4 at room temperature (over 10,000 h). The electrodes consist of mixtures of commercial AG-3 carbon with 5-10 wt. % of the organic catalyst and 15 wt. % of the fluoroplast. For electrode fabrication the carbon is soaked with the solution of organic catalyst in a suitable solvent, carefully mixed, and after elimination of the solvent heated for 20 min to 800-900°C in inert-gas atmosphere.

Polarization curves for oxygen reduction at cobalt-chelate-promoted carbon electrodes which were or were not heat-treated are reported in Fig. 1. The heat treatment has no effect on the starting activity of the catalysts examined, but substantially influences their operating stability (Fig. 2). At a current density of 10 mA/cm^2 ($\phi=0.77$ V), the electrodes already have functioned for 10,000 h, and at 30 mA/cm^2 ($\phi=0.75$ V) for 2500 h, and continue to function with unchanged characteristics.

The heat treatment at high temperatures appears to cause destruction of the organic complex [6]. The destruction may be attended by the formation of radicals which can polymerize yielding a polyconjugate structure. X-ray analysis indicates that after the action of heat upon cobalt chelates one obtains compounds containing at least three phases: $\beta\text{-Co}$, carbon, and a phase at $\theta \sim 14^\circ$ which has a very broad line, or halo. Elementary analysis indicates that the amount of carbon decreases by 10%, that of hydrogen by a factor of two. For instance, the empirical formula of the original CoTMPP is $\text{C}_{51}\text{H}_{42}\text{O}_4\text{N}_4\text{Cl}_2\text{Co}_1$, that of the

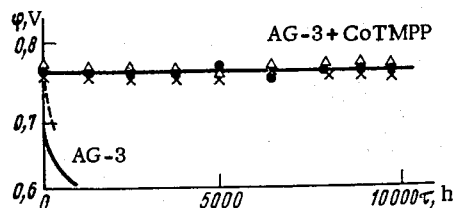


Fig. 2

Fig. 2. Prolonged operation of carbon-based oxygen electrodes promoted with 5 wt. % of CoTMPP and heat-treated at 800°C, in 4.5 N H₂SO₄ (20°C) at $i = 10 \text{ mA/cm}^2$. Dashed line: Norite + 5 wt. % CoTMPP, 3 N H₂SO₄, 30°C. The curve is plotted from data reported in [4].

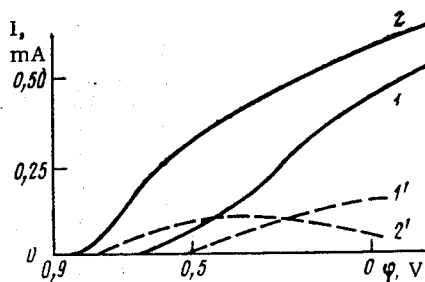


Fig. 3

Fig. 3. Polarization curves for O₂ reduction at a disk electrode coated with a thin layer of AG-3 (1) or of AG-3 + 5 wt. % CoTMPP heated in an inert atmosphere to 800°C (2), and the corresponding limiting currents of H₂O₂ oxidation at the ring (1', 2') in 0.1 N H₂SO₄; $m = 960 \text{ rpm}$.

material heated to 800°C is C₄H₂O₄N₄CO₁. The chemical stability of the heat-treated catalysts in sulfuric acid is appreciably higher than that of the original compounds.

From the results obtained one can suggest that polymetric compounds involving Co are produced during the heat treatment. It is precisely the new organic complex obtained after heat treatment which made it possible to create sufficiently active oxygen electrodes giving stable performance over a prolonged period of time in strongly acidic electrolyte. The studies showed that the heat treatment does not lead to any change in the basic parameters of the porous active layer, i.e., the overall porosity or the ratio between liquid pores and gas pores. On the other hand, there is a substantial increase in the rate of heterogeneous H₂O₂ decomposition on the heat-treated catalyst powders as compared to catalyst which was not heated. This seems to be an indication for the determining role of microkinetic factors in the stabilization of electrochemical characteristics of porous gas electrodes.

The ring-disk electrode [7] was used to conduct experiments at extremely thin layers of AG-3-CoTMPP mixtures applied to a pyrographite disk [8]. It can be seen from the results of polarization measurements (Fig. 3) that the reduction of molecular O₂ in the presence of heat-treated CoTMPP is much faster; this is seen from the shift of the curve toward more positive potentials. The rates of the partial reactions of the overall process of O₂ reduction were determined with the aid of the method described in [9]. The calculations showed that O₂ reduction at heat-treated CoTMPP, just as at AG-3, goes via the intermediate formation of H₂O₂: $\text{O}_2 \xrightarrow{k_1, +2e} \text{H}_2\text{O}_2 \xrightarrow{k_2, +2e} \text{H}_2\text{O}$. But the rate constants of O₂ reduction to hydrogen peroxide increase by an order of magnitude as a result of the heat treatment. On the other hand, there also is a substantial acceleration of the further transformation of hydrogen peroxide. This results in a lower H₂O₂ concentration in the pores of the active layer and in a stabilization of the operation of the oxygen electrodes in acidic electrolyte.

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