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Studies of Selectivity of Oxygen Reduction Reaction in Acidic Electrolyte on Electrodes Modified by Products of Pyrolysis of Polyacrylonitrile and Metalloporphyrins

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Abstract—The rotating disk electrode technique was used to study in 0.5 M H_2SO_4 catalytic properties of products of pyrolysis of the metal-free polyacrylonitrile/carbon black composite, polyacrylonitrile/iron/carbon black composite, and also supported pyropolymers of Co(II) tetramethoxyphenyl porphyrine (CoTMPP) and Fe(III) tetramethoxyphenyl porphyrin chloride (FeTMPPCl). It is shown that the metal-free polyacrylonitrile/carbon black composite catalyzes the oxygen reduction reaction via the parallel path. Addition of up to 2% of Fe into the composite results in abrupt growth of the catalytic activity and share of the four-electron reaction, which provides the parallel–serial reaction path. The parallel reaction with no further catalytic conversion of H_2O_2 occurs on catalysts of the CoTMPP/Vulcan XC72 and FeTMPPCl/Vulcan XC72 series. The chemical composition is one of the key factors affecting activity and selectivity of CoTMPP/Vulcan XC72 catalysts. An increase in the precursor content from 5 to 30% is accompanied by an increase in selectivity k_1/k_2 from 0.14–0.30 to 0.5–1.7, where k_1 is the rate constant of the reaction of O_2 reduction to H_2O, k_2 is the rate constant of the reaction of O_2 reduction to H_2O_2.

Keywords: oxygen reduction, catalyst, acidic medium, Co tetramethoxyphenyl porphyrin, Fe(III) tetramethoxyphenyl porphyrin chloride, polyacrylonitrile, RRDE, selectivity

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INTRODUCTION

The new trend in the field of electrocatalysis was embarked on in 1960-ies owing to discovery of catalytic activity of molecules of metal phthalocyanines in the oxygen reduction reaction in alkaline electrolytes [1, 2] and was developed first in studies in 1970-ies [3–6], when products of pyrolysis of N_4-complexes were first suggested as replacement of platinum catalysts, and then, in mid-1980-ies, [7] were followed by development of catalysts based on polyacrylonitrile and simple Co and Fe salts. Despite the fact that carbon catalytic systems based on pyrolysis products with the composition of C–N–M (M = Fe, Co, Cu) continue to be of high priority [8], there is a trend for searching cheap metal–free catalysts based on doped carbon materials [9]. As opposed to catalysts of the C–N–M type that were demonstrated experimentally to be a relatively efficient replacement of Pt in cathodes of H_2–O_2 fuel cells with polymer electrolyte [10, 11], there are no such results as yet for metal–free catalysts. The most important aspect determining practical applicability of catalysts is the degree of their selectivity in the reaction of O_2 reduction directly to water. The highest catalytic activity and selectivity is manifested by Pt-containing catalytic systems [12–14]. Less efficient characteristics are observed for chalcogenides and catalysts of the C–N–M type. As shown earlier in [15] and pointed out in this source, in a short literature review, that the apparent selectivity of platinum–free catalysts, such as Se/Ru/C [16], $CoSe_2$/C [17], CN_x [18], determined using the rotating disk electrode and rotating ring–disk electrode (RRDE) methods grows at an increase in the catalyst layer thickness. The RRDE method was used in [19] to study O_2 reduction in 0.5 M H_2SO_4 on Ketjenblack EC-300 carbon black, the metal–free product of pyrolysis of the polyaniline(PANI)/C composite, Co-PANI/C, Fe/PANI/C, Fe–Co-PANI/C composites, and Pt/C E-TEK catalyst in 0.1 M $HClO_4$ and determine the yield of H_2O_2. The share of H_2O_2 on the Ketjenblack EC-300 carbon black was 60–80%, the potential of the start of O_2 reduction was $E < 0.5$ V[1]. Thermal treatment of carbon black results in a certain

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[1] All potentials are presented vs. the reversible hydrogen electrode (RHE).

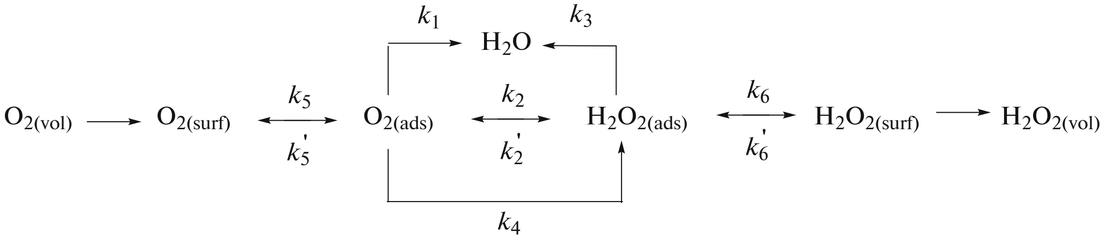

Fig. 1. Scheme of the parallel–serial oxygen electroreduction reaction. The scheme: k_1 is the rate constant of the reaction of $O_2 + 4e + 4H^+ \rightarrow 2H_2O$; k_2 is the rate constant of the reaction of $O_2 + 2e + 2H^+ \rightarrow H_2O_2$; k_3 is the rate constant of the reaction of $H_2O_2 + 2e + 2H^+ \rightarrow 2H_2O$; k_4 is the rate constant of the reaction of $2H_2O_2 \rightarrow O_2 + 2H_2O$; k_5, k_5' are the rate constants of O_2 adsorption and desorption; k_6, k_6' are the rate constants of H_2O_2 adsorption and desorption.

decrease in the yield of H_2O_2 to 40%. A decrease is observed in formation of H_2O_2 to 12–20% on the metal–free PANI/C composite, to less than 10% on metal–containing composites, and less than 1% for the Fe–Co-PANI/C composite. Studies of the effect of the temperature of pyrolysis of the Fe–Co-PANI/C composite in the range of 400–1000°C showed that its optimum value is in the range of 850–950°C. It was shown that the effect of the Fe–Co-PANI/C catalyst loading on the value of selectivity in the O_2 reduction reaction is negligible due to the high share of the H_2O yield comparable with that on the platinum catalysts.

Catalysts of the $Co_{0.5}Mo_{0.5}N_y$ type supported on N-doped carbon materials were synthesized in [20] with the potential of the start of O_2 reduction being 0.8 V and the yield of H_2O_2 in the range of $E = 0.1$–0.6 V being less than 16%.

It was shown in [21] in the studies of O_2 reduction on polypyrrole films in 0.5 M H_2SO_4 using the RRDE technique that the values of k_1, k_2, and k_3 (see Fig. 1) are 2.1×10^{-5}, 2.0×10^{-4}, and 7.9×10^{-6} m/s, accordingly. It was demonstrated by determining the rate constants of partial reactions on chalcogenides of the $(Ru_{1-x}Mo_x)_ySeO_z$ type in [22], same as in [21], that the k_1/k_2 ratio varies from 10 to 30 at the yield of H_2O_2 below 4%. Here, the values of k_1, k_2, and k_3 as dependent on the potential vary in the ranges of 2×10^{-6} to 4×10^{-4}, 1×10^{-5} to 1×10^{-7}, and 1×10^{-6} to 4×10^{-6} m/s, accordingly. Close values of $k_1/k_2 \sim 10$ were obtained in [23] for catalysts of the $Ru_xS_y(CO)_n$ type.

It was shown in [24] at the example of the catalyst of 7% of Fe(III) tetramethoxyphenyl porphyrin chloride (FeTMPPCl)/Vulcan XC72 that the condition of $k_1/k_2 > 1$, when the O_2 reduction reaction occurs predominantly via the direct path, is observed only at $E > 0.6$ V.

The authors of [25] studied the effect of the content of Fe (from tens to 10^4 ppm) and pyrolysis temperature from 400 to 1000°C on the yield of H_2O_2 for catalysts based on supported Fe acetate and FeTMPPCl. It was shown that there is a certain inverse dependence between the concentration of Fe and yield of H_2O_2: the share of H_2O_2 is >20% at the Fe concentration <50 ppm, but its yield can be decreased to <5% at the Fe concentration of >2000 ppm. A brief literature review [26] showed that there is a considerable spread of the H_2O_2 yield (from 0 to 65%) in acidic media for Fe- and Co-containing catalytic systems even at their close composition.

The aim of this work consisted in studying the effect of the composition of catalysts obtained by pyrolysis of metalloporphyrins and polyacrylonitrile on selectivity of the O_2 reduction process in 0.5 M H_2SO_4. Selectivity was estimated on the basis of the yield of H_2O_2 (%) and values of the k_1/k_2 ratio of constants. The composition of catalysts was varied by application of (1) three different nitrogen–containing precursors, polyacrylonitrile, Co and Fe porphyrins; (2) different metals, such as Co and Fe, or metal–free systems; (3) different precursor amounts on the carbon black support; and, finally, (4) different postpyrolytic treatment: washing in the 0.5 M H_2SO_4 and 0.5 M H_2SO_4 + 1.8 M H_2O_2 solutions or without additional treatment. The obtained results allowed comparing the efficiency of the studied materials of different composition as catalysts for power sources of electrochemical synthesis of H_2O_2.

EXPERIMENTAL

The chemicals used for preparation of solutions and suspensions were H_2SO_4 (reagent grade, Sigma Tech), H_2O_2 (especially pure grade, Tekhprom), CH_3Cl (chemically pure grade, Ekos-1), C_2H_5OH (rectificate, 96%). The precursors for catalyst synthesis were polyacrylonitrile (PAN) $(–CH_2–CH(CN)–)_n$ (150000 g/mol, Sigma Aldrich); 1.1'-diacetyl ferrocene (DAF) $C_{14}H_{14}FeO_2$ (270 g/mol, INEOS RAS); cobalt(II) tetramethoxyphenyl porphyrin (CoTMPP) $C_{48}H_{36}CoN_4O_4$ (792 g/mol, Sigma Aldrich); iron(III) tetramethoxyphenyl porphyrin chloride $C_{48}H_{36}FeClN_4O_4$ (824 g/mol, Sigma Aldrich). The supports for catalysts used were carbon blacks Ketjenblack EC-600 (Akzo-Nobel) and Vulcan XC72R (Cabot).

The 40% PAN/Ketjenblack EC-600 and 38% PAN/2% DAF/Ketjenblack EC-600 composites were synthesized by depositing 1,1'-diacetyl ferrocene and/or polyacrylonitrile onto the surface of the Ketjenblack EC-600 carbon black, oxidizing the whole in air at 250°C for 6 h, and carbonizing it in vacuum of 10^{-5} torr at the temperature of 900°C for 2 h. The technique of synthesis of catalysts of the CoTMPP/Vulcan XC72 or FeTMPPCl/Vulcan XC72 series is described in [27]: the solution of metalloporphyrin in chloroform was mixed with the suspension of the Vulcan XC72R carbon black in ethanol; then the liquid phase was evaporated and the whole was pyrolyzed in the inert atmosphere at 850°C (2 h). Some catalysts were washed in 0.5 M H_2SO_4 at 80°C or in 0.5 M H_2SO_4 + 1.8 M H_2O_2 at 80°C to remove soluble pyrolysis products (metallic Co/Fe and their oxides) and then were repeatedly washed by deionized water. The washed powder was left to dry overnight in a vacuum chamber at the temperature of 80–90°C.

The surface composition was determined using the method of X-ray photoelectron spectroscopy (XPS) on a Auger microscope (Vacuum Generators). The composition of catalysts is shown in Table 1.

Electrochemical measurements were carried out in a three–electrode thermostated glass cell. Platinum gauze was used as an auxiliary electrode. The reference electrode was a mercury sulfate reference electrode, $Hg/Hg_2SO_4/0.5$ M H_2SO_4, with the potential of +0.695 V. The working electrode was a rotating ring disk electrode consisting of a glassy carbon disk and a platinized Pt ring positioned coaxially. The diameter of the glassy carbon disk was 0.5 cm; the inner and outer Pt ring diameters were 0.65 and 0.75 cm, accordingly. The geometrical surface area of the disk electrode was ~0.2 cm^2, the area of the ring electrode was ~0.11 cm^2. Synchronous current measurement on the disk and ring electrodes was carried out using a Pine Instrument bipotentiostat. Before measurements, the Pt electrode was activated by hours long cyclic cathodic–anodic polarization in the range of potentials of 0.05–1.5 V in the solution of 0.5 M H_2SO_4 at the temperature of 25°C. The experimental value of efficiency coefficient N is 0.25 [28]. Analysis of the obtained experimental data was carried out according to equation (1), according to the scheme in Fig. 1 [29]. Equation (2) was used to calculate the yield of H_2O_2.

$$\frac{I_D N}{I_R} = 1 + 2\frac{k_1}{k_2} + \frac{k_3 + (k_3 + k_4)\left(1 + 2\frac{k_1}{k_2}\right)}{0.62 D_{H_2O_2}^{2/3} \nu^{-1/6}} \omega^{-1/2}, \quad (1)$$

$1 + 2\frac{k_1}{k_2} = I$ is the cutoff on the y-axis.

$\frac{k_3 + (k_3 + k_4)\left(1 + 2\frac{k_1}{k_2}\right)}{0.62 D_{H_2O_2}^{2/3} \nu^{-1/6}} = S$ is the slope of the line,

$$\%\ (H_2O_2) = \frac{2 I_R/N}{I_D + I_R/N} \times 100. \quad (2)$$

The working electrode was prepared by application of 200 μg/cm^2 of the catalyst from the suspension onto the disk electrode. The suspension was prepared by ultrasonic dispersion of 2 mg of the catalyst in 1 ml of ethanol with the additive of Nafion as a binder at the amount of 5% of the sample weight. The RRDE measurements were carried out in 0.5 M H_2SO_4 at 25°C: solubility of O_2 $c_{O_2} = 1.1$ mol/m^3; diffusion coefficient of O_2 $D_{O_2} = 1.4 \times 10^{-9}$ m^2/s; solution viscosity $\nu = 1.0 \times 10^{-6}$ m^2/s [30].

RESULTS AND DISCUSSION

Reaction Path on PAN/Carbon Black Metal–Free Composites

Figure 2 shows polarization curves of O_2 reduction on a disk electrode on which a layer of the 40% PAN/Ketjenblack EC-600 catalyst is applied and oxidation currents of the formed H_2O_2 on the ring Pt electrode (I_R) at different electrode rotation rates. The values of I_R/N correspond by their absolute value to the current values of the two–electron reaction of O_2 reduction to H_2O_2 on the disk electrode. The starting potential of O_2 reduction on the composite does not exceed 0.65 V, which points to the low activity of the material and its unsuitability as a cathode material, which, however, does not exclude the possibility of its application for electrochemical synthesis of H_2O_2. Analysis of the obtained experimental data according to equation (1) allows estimating the value of selectivity expressed as the ratio of reaction constants k_1/k_2. As seen from Table 2, k_1/k_2 is 0.17–0.25 in the range of potentials of 0.1–0.4 V. This indicates that the rate constant of O_2 reduction to H_2O_2 (k_2) by far exceeds the rate constant of O_2 reduction to H_2O (k_1) in the whole studied potential range. As follows from the reaction scheme in Fig. 1, the absence of the slope in the plot of the $I_D N/I_R, \omega^{-0.5}$-dependence (not shown

Table 1. Analysis of the surface composition of the CoTMPP-based catalysts by means of the XPS technique

No.	Catalyst	Line	E_{bond}, eV	c, at %	c_{Σ}*, at %
1	5% CoTMPP/Vulcan XC72	C 1*s*	284.9	99.3	99.3
		N 1*s*	–	–	–
		O 1*s*	533.3	0.50	0.50
		Co 2*p*	780.0	0.05	0.05
2	5% CoTMPP/Vulcan XC72 treated in 0.5 M H_2SO_4	C 1*s*	284.8	98.8	98.8
		N 1*s*	–	–	–
		O 1*s*	532.4	1.01	1.01
		Co 2*p*	–	–	–
3	15% CoTMPP/Vulcan XC72	C 1*s*	284.3	97.7	97.7
		N 1*s*	399.1	0.70	0.70
		O 1*s*	531.7	1.15	1.15
		Co 2*p*	780.2	0.26	0.26
4	15% CoTMPP/Vulcan XC72 treated in 0.5 M H_2SO_4	C 1*s*	283.7	96.6	96.6
		N 1*s*	398.5	1.08	1.08
		O 1*s*	531.2	1.83	1.83
		Co 2*p*	779.2	0.14	0.14
5	30% CoTMPP/Vulcan XC72	C 1*s*	284.6	95.3	95.3
		N 1*s*	398.7	1.15	2.04
			401.0	0.89	
		O 1*s*	531.9	1.80	1.80
		Co 2*p*	780.2	0.48	0.55
			786.1	0.07	
6	30% CoTMPP/Vulcan XC72 treated in 0.5 M H_2SO_4	C 1*s*	284.5	94.5	94.5
		N 1*s*	398.6	1.16	1.19
			400.8	0.75	
		O 1*s*	531.7	2.73	2.73
		Co 2*p*	779.9	0.44	0.52
			783.4	0.08	
			785.0	0.02	
7	30% FeTMPPCl/Vulcan XC72 treated in 0.5 M H_2SO_4+1.8 M H_2O_2	C 1*s*	284.5	93.26	93.26
		N 1*s*	399.6	0.9	0.9
		O 1*s*	534.4	0.68	5.83
			532.6	3.43	
			531.1	1.72	
		Fe 2*p*	–	–	–

* Without account for the content of sulfur.

Table 2. Ratio of rate constants k_1/k_1 for the 40% PAN/Ketjenblack EC-600 catalyst

E, V	k_1/k_2
0.45	0.40
0.4	0.25
0.3	0.17
0.2	0.20
0.1	0.25

here) allows concluding that the catalyst does not promote further reactions with participation of H_2O_2 formed on its surface. The latter fact also points to the possibility of using the metal–free composite for synthesis of H_2O_2. Thus, supported metal–free PAN pyropolymers in acidic media provide to be catalysts of low activity promoting the oxygen reduction reaction via the parallel path with predominant formation of H_2O_2.

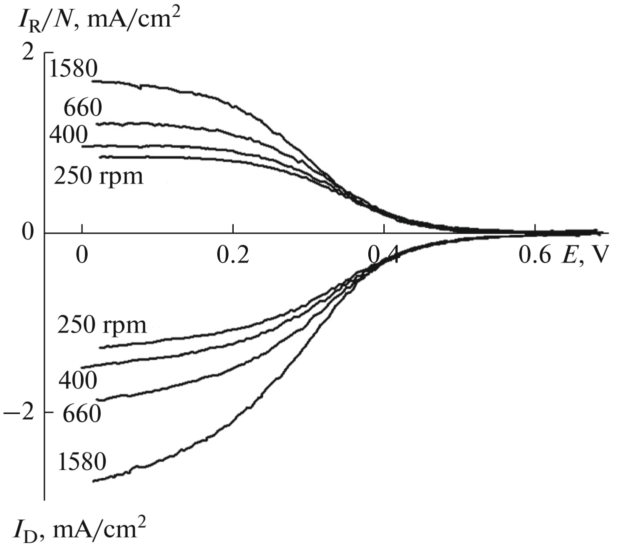

Fig. 2. Polarization curves of O_2 reduction (I_D) on 40% PAN/Ketjenblack EC-600 and currents of H_2O_2 oxidation (I_R). 0.5 M H_2SO_4. 25°C.

Reaction Path on PAN/Fe/Carbon Black Composites

Figure 3a shows, by analogy with Fig. 2, the results of studies of the kinetics of O_2 reduction on the composite catalyst of 38% PAN/2% DAF/Ketjenblack EC-600. As seen in Fig. 3a, the starting potential of O_2 reduction on the catalyst is ~0.85 V, i.e., ~0.4 V more positive as compared to the metal–free composite. As follows from Fig. 3b that shows the plots of the $I_DN/I_R,\omega^{0.5}$-dependence, these data can be described by equation (1) with a nonzero slope. This points to occurrence of the further chemical and/or electrochemical conversions with participation of the formed H_2O_2. The cutoffs on the y-axis that are equal to $1 + 2k_1/k_2$ were used to calculate the values of k_1/k_2 (Table 3). As seen from Table 3, the k_1/k_2 ratio in the whole range of potentials from 0.2 to 0.75 V exceeds 1.5; at potentials to the negative of 0.6 V, a gradual increase in selectivity is observed at an increase in polarization of the electrode. It seen from comparison of the k_1/k_2 values for the metal–free (Table 2) and Fe-containing (Table 3) composites at similar potentials that addition of 2% of Fe into the composite results in an increase in selectivity by more than an order of magnitude: at $E = 0.4$ V, the value of k_1/k_2 is 4.5 for the catalyst of 38% PAN/2% Fe/Ketjenblack EC-600 as compared to 0.25 for the 40% PAN/Ketjenblack EC-600 composite. Thus, the oxygen reduction reaction on the composite PAN/Fe/carbon black catalyst occurs via the parallel–serial path according to the scheme in Fig. 1 with predominant formation of H_2O via the direct four–electron reaction. Here, the composite also manifests a certain catalytic activity with respect to H_2O_2 formed on its surface.

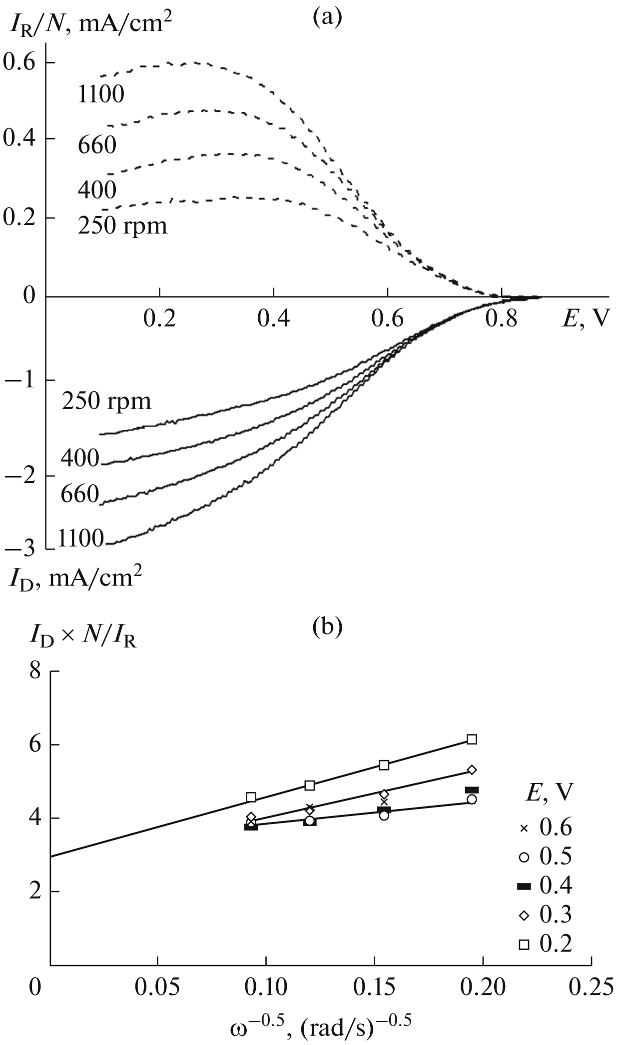

Fig. 3. (a) Polarization curves of O_2 reduction (I_D) on the 38% PAN/Fe/Ketjenblack EC-600 catalyst and currents of H_2O_2 oxidation (I_R). 0.5 M H_2SO_4, 25°C. (b) $I_DN/I_R,\omega^{0.5}$-dependence for 38% PAN/2% Fe/Ketjenblack EC-600. 0.5 M H_2SO_4, 25°C.

Reaction Path on CoTMPP/Vulcan XC72 Catalyst

The results of studying the kinetics and selectivity of O_2 reduction on a series of CoTMPP/Vulcan XC72 catalysts containing 5, 15, and 30% metal porphyrins enumerated from 1 to 6 according to Table 1 are shown in Fig. 4a. As opposed to alkaline media, where the polarization curve and selectivity weakly depend on the amount of the initial precursor [27], an increase in the metal porphyrin amount in acidic electrolyte leads to a significant decrease in the overpotential of the oxygen reduction reaction: polarization curves are

Table 3. Ratio of rate constants k_1/k_1 for the 38% PAN/2% Fe/Ketjenblack EC-600 catalyst

E, V	k_1/k_2
0.75	3.0
0.7	2.1
0.6	1.5
0.5	2.6
0.4	4.5
0.3	6.0
0.2	8.3

Table 4. Ratio of reaction constants k_1/k_2 for catalysts nos. 1–6 as dependent on the electrode potential

E, V	k_1/k_2					
	no. 1	no. 2	no. 3	no. 4	no. 5	no. 6
0	0.30	0.28	0.52	0.39	0.52	0.61
0.1	0.30	0.19	0.57	0.43	0.60	0.70
0.2	0.24	0.10	0.50	0.38	0.68	0.86
0.3	0.16	0.06	0.42	0.36	0.83	0.91
0.4	0.14	0.01	0.39	0.39	1.10	1.13
0.5	0.14	0.00	0.37	0.40	1.52	1.23
0.6	–	–	0.37	0.35	1.54	–
0.7	–	–	–	–	1.70	1.59

Table 5. Ratio of reaction constants k_1/k_2 for the 30% FeTMPPCl/Vulcan XC72 catalysts as dependent on the electrode potential

E, V	k_1/k_2	
	washed in 0.5 M H_2SO_4	washed in 0.5 M H_2SO_4 + 1.8 M H_2O_2
0.7	–	2.4
0.6	4.3	3.2
0.5	4.6	3.2
0.4	5.2	3.5
0.3	5.4	3.7
0.2	5.7	4.2

shifted towards more positive potentials, the current values measured on the disk electrode increase and those on the ring decrease. Calculation of the yield of H_2O_2 according to equation (2) shows that: (1) the catalyst containing 5% CoTMPP catalyzes the reaction predominantly with formation of H_2O_2; its yield decreases to ~75%, as the potential shifts towards the cathodic region; (2) the 15% CoTMPP/Vulcan XC72 catalyst catalyzes the oxygen reduction reaction with the yield of H_2O_2 up to 70% practically in the whole region of potentials; (3) on the 30% CoTMPP/Vulcan XC72 catalyst, the yield of H_2O_2 reaches 40% at low polarization and increases to 60% in the cathodic polarization range. Similar results were obtained by the authors of [24] for products of FeTMPPCl pyrolysis supported on carbon black. As seen in Fig. 4b, the curves of the dependence of the yield of H_2O_2 on the potential are complex and draw together at high cathodic potentials. The washing of catalysts in acid results in a certain increase in the yield of H_2O_2. Analysis of the $I_DN/I_R,\omega^{-0.5}$-dependence (Fig. 4c) shows that the plots can be described with a certain error using line equation (1) parallel to the x-axis. Therefore, the sum of rate constants of the reactions of H_2O_2 reduction to H_2O (k_3) and catalytic decomposition of H_2O_2 (k_4) is close to zero and the oxygen reduction reaction on the studied series of catalysts yields two stable compounds: water (with rate constant k_1) and hydrogen peroxide (with rate constant k_2). The values of constant ratio k_1/k_2 obtained by extrapolation of linear dependences to the infinite rotation rate are presented in Table 4. At the constant potential of 0.4 V, selectivity of reaction on catalysts untreated in acid grows from 0.14 to 1.1 at an increase in the precursor content from 5 to 30%. Thus, the catalyst with a low content of pyrolysis products manifests the values of selectivity and the starting potential of O_2 reduction close to metal–free PAN/Ketjenblack EC-600 composites. The catalyst with the optimum content of 30% CoTMPP/Vulcan XC72 is inferior by its activity and selectivity as compared to Fe–containing 38% PAN-900/2% Fe/Ketjenblack EC-600 catalysts and, as shown further, to 30% FeTMPPCl/Vulcan XC72.

Reaction Path on FeTMPPCl/Vulcan XC72 Catalyst

Figure 5a compares polarization curves of O_2 reduction on the catalysts with the similar initial composition with different conditions of postpyrolytic treatment. The results shown in Fig. 5a and in Table 5 point to the negative effect of H_2O_2 on activity and selectivity of the O_2 reduction reaction: The halfwave potential shifts by ~0.04 V towards less positive potentials and the value of the k_1/k_2 ratio decreases from 5.2 to 3.5 at the potential of 0.4 V. Here, monotonous growth of selectivity is observed at a negative shift in the potential for the 30% FeTMPPCl/Vulcan XC72 catalyst, same as for the 38% PAN/2% DAF/Ketjenblack EC-600 composite (Table 3) and 30% CoTMPP/Vulcan XC72 catalysts (Table 4).

As follows from Fig. 5b showing the plots of the $I_DN/I_R,\omega^{-0.5}$-dependence according to equation (1), the products of Fe porphyrin pyrolysis catalyze the oxygen reduction reaction via the parallel path and promote neither the catalytic decomposition of the formed H_2O_2, nor its electrochemical reduction. However, the result we obtained differs from the data

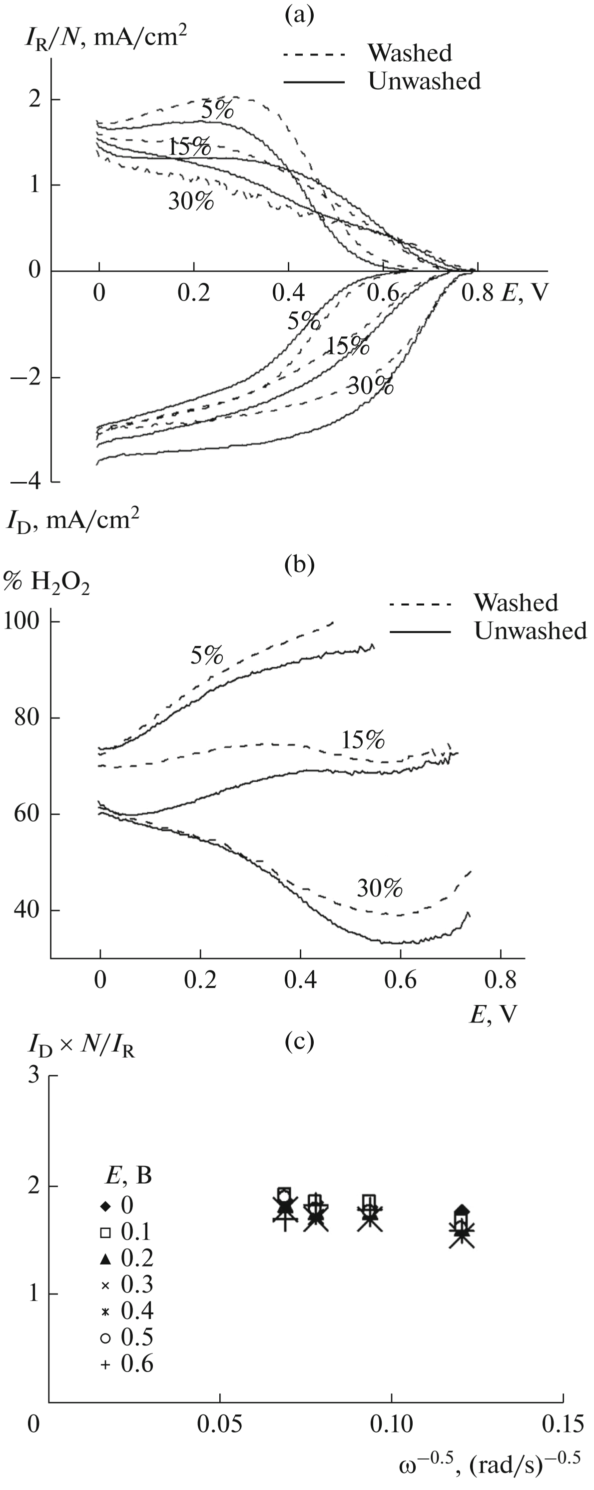

Fig. 4. (a) Polarization curves of O_2 reduction (I_D) on samples nos. 1–6 and currents of H_2O_2 oxidation (I_R). 0.5 M H_2SO_4, 1580 rpm, 25°C. (b) Dependence of the yield of H_2O_2 on the electrode potential for the catalysts of 5, 15, 30% CoTMPP/Vulcan XC72 treated and untreated in 0.5 M H_2SO_4. 0.5 M H_2SO_4, 25°C. (c) $I_DN/I_R,\omega^{0.5}$-dependence for the washed catalyst of 15% CoTMPP/Vulcan XC72 (no. 4, Table 1). 0.5 M H_2SO_4, 25°C.

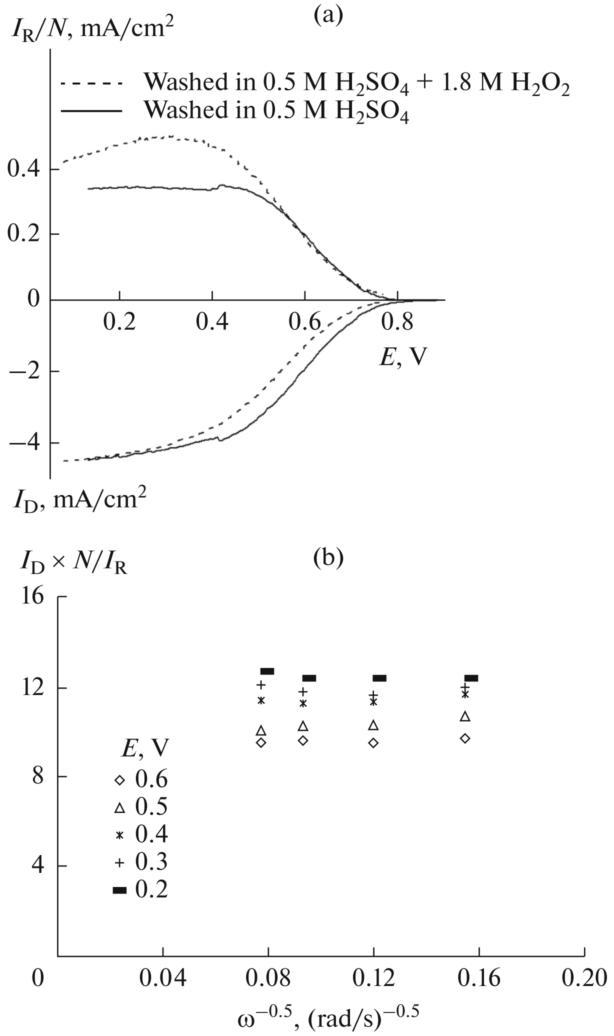

Fig. 5. (a) Polarization curves of O_2 reduction (I_D) on the 30% FeTMPPCl/Vulcan XC72 catalysts washed in 0.5 M H_2SO_4 and in 0.5 M H_2SO_4+1.8 M H_2O_2 and currents of H_2O_2 oxidation (I_R). 0.5 M H_2SO_4, 1580 rpm, 25°C. (b) $I_DN/I_R,\omega^{-0.5}$-dependence for the 30% FeTMPPCl/Vulcan XC72 catalyst washed in 0.5 M H_2SO_4. 0.5 M H_2SO_4, 25°C.

of work [24], where it was shown that the slope of the plot for the 7% FeTMPPCl/Vulcan XC72 catalyst is (700°C) higher than zero. Reduction of H_2O_2 on this system was experimentally confirmed by direct measurement of the corresponding polarization curves.

CONCLUSIONS

It follows from the provided experimental data in acidic media that:

(1) Metal–free catalysts of PAN/carbon black composites reduce O_2 via the parallel path with selectivity $k_1/k_2 = 0.17–0.25$ and do not promote the fur-

ther reactions with participation of the forming H_2O_2. Such catalysts are unsuitable for power sources but can be used for electrochemical synthesis of H_2O_2.

(2) Fe-containing PAN/Fe/carbon black catalysts manifest even at low Fe content (<2%) significant catalytic activity in the oxygen reduction reaction via the parallel–serial path with selectivity $k_1/k_2 = 1.5–8.3$ as dependent on the electrode potential. These cheap catalysts, if their activity is enhanced, can be considered as promising catalysts for fuel cell cathodes.

(3) An increase in the CoTMPP content from 5 to 30% on the surface of carbon black Vulcan XC72 results in a considerable increase in the catalytic activity and a drastic decrease in the yield of H_2O_2. Irrespective of the precursor content, the catalysts of the CoTMPP/Vulcan XC72 series catalyze the oxygen reduction process via the parallel path with the maximum selectivity of $k_1/k_2 = 1.7$. Catalyst treatment in 0.5 M H_2SO_4 for 4 h at 80°C results in a certain decrease in activity and selectivity. The catalysts with the precursor content of 5% can be of interest for electrochemical synthesis of H_2O_2 and provide the product yield close to 100%. It is recommended to use catalysts with porphyrin content of at least 30% in fuel cells. Here, it is necessary to carry out special corrosion tests in acidic media.

(4) The 30% FeTMPPCl/Vulcan XC72 catalysts provide the flow of the oxygen reduction reaction via the parallel path with the selectivity of $k_1/k_2 = 2.4–5.7$ and are more effective than Co-containing catalysts.

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