Peer-reviewed version available at *Catalysts* **2020**, *10*, 892; doi:10.3390/catal10080892

Carbon nanotube modified by (O, N, P) atoms as effective catalysts for electroreduction of oxygen in alkaline media

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Abstract

The influence of the type and amount of oxygen (O), nitrogen (N), and/or phosphorus (P) heteroatoms on the surface of carbon nanotube (CNT) on stability and catalytic activity in the oxygen reduction reaction (ORR) was investigated in alkaline media. It is shown that the functionalization of CNT leads to the growth of the electrochemically active surface and to an increase in the activity in ORR. At the same time, a decrease in stability is observed after the functionalization of CNT under accelerated corrosion testing in an alkaline media. These results are most significant on CNT after functionalization in HNO_3 due to the formation of a large number of structural defects. However, the subsequent doping by N and / or P atoms provides a further activity increase and enhances the corrosion stability of CNT. Thus, as shown by the studies of characteristic parameters (S_{EAS}, $E_{1/2}$, corrosion stability), CNT doped with N and NP are a promising catalytic system that can be recommended for use as fuel cell cathodes. An important condition for effective doping is the synthesis of carboxyl and carbonyl oxygen containing group on the surface of CNT.

Key words: Carbon nanotube; Functionalization; Heteroatoms; Electrochemically active surface; Oxygen reduction reaction; Corrosion stability; Alkaline media

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1. INTRODUCTION

The development of active and stable catalysts for the cathodic oxygen reduction reaction is a priority problem for the production of fuel cells (FC) and metal-air batteries [1, 2]. Among such systems, alkaline FC operating with a high efficiency at the atmospheric pressure in a wide temperature range are of particular importance [3].

A number of studies have shown that CNT are a promising material for FC cathodes due to such properties as corrosion stability, large specific surface area, and high electric conductivity [1, 4]. However, the initial CNT have low activity in ORR, therefore, it is necessary to modify their surface in order to create active centres (AC) [5]. The most common approaches for FC development are functionalization (oxidation) of the CNT surface using acids or bases and doping with heteroatoms. The functionalization promotes formation of functional oxygen-containing groups on the surface of CNT that provide an increase in activity in ORR [6 - 8]. The introduction of heteroatoms, such as nitrogen, phosphorus, sulfur, etc., into the structure of CNT leads to a further activity increase as a result of a change in the electronic structure of the carbon material [9]. For example, during the doping by nitrogen that acts as an electron donor in the carbon material, the Fermi level shifts into the conduction band, which makes all nitrogen-doped carbon material metallic. This facilitates the transfer of electrons to adsorbed oxygen molecules. The difference in electronegativity, regardless of whether the dopants have a higher (as N) or lower (as B, P, S) electronegativity, than that of carbon, causes a change in the charge distribution favoring O_2 adsorption [10, 11]. This promotes the breaking of O-O bonds in the oxygen molecule and increases the selectivity of the reaction of oxygen reduction to water. A number of studies [12, 13] reported that carbon doped both by N and P atoms exhibits higher electrocatalytic activity in ORR and demonstrates improved oxygen adsorption, which, according to the authors, may be due to a synergistic interaction between N and P or to the effect of just the combination of single N and P atoms. In Ref. [12], the doping of CNT by nitrogen and phosphorus atoms was carried out directly during the synthesis of CNT (Ar, 760-840^{0}C) in the presence of benzylamine and triphenylphosphine (TPP) as sources of nitrogen and phosphorus, respectively, and ferrocene as a catalyst. In Ref. [13], a post-treatment method was adopted to prepare dual-doped carbon by heat treatment (800^{0}C) of mesoporous carbon in an inert zone, where TPP and dicyandiamide (DCDA) were used as P and N precursors. The total amount (at.%) of N and P on the surface of the carbon material under these conditions ranged from 4.08 (simultaneous doping) and 4.1 (first N, then P) to 3.74 (first doped with P, then N). Here, an increase in activity in ORR was observed with the introduction of two atoms, especially in the latter case. The authors attribute this to the fact that in the presence of P, N atoms are introduced in the graphitic-N positions that are most active in ORR. Possibly, this type of nitrogen is formed during partial replacement of phosphorus. However, these assumptions require additional confirmation and the presence of oxygen-containing groups on the surface should also be taken into account.

Much less attention is paid to the corrosion stability of CNT and influence of the amount and method of doping on stability, as well as the necessity of pre-functionalization [14]. Such studies are required because structure defects can be formed in the process of functionalization and doping, which cause a decrease in the BET surface area and pore size and surface area.

The aim of this study is to determine the effect of modification of CNT by oxygen, nitrogen and/or phosphorus atoms on stability and activity in the oxygen reduction reaction in alkaline electrolytes and to synthesize a catalyst free of precious metals for use as a fuel cell cathode.

2. EXPERIMENTAL (MATERIALS AND METHODS)

CNTs were bought from Nanotechcenter LLC (Tambov). Melamine and TPP were used as N and P precursors. Solutions of NaOH or concentrated HNO_3 were used for functionalization.

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Electrochemical methods.

The studies were carried out by electrochemical methods. Cyclic voltammograms (CV) were obtained at a 100 mV/s scan rate on a stationary electrode. Measurements on a rotating disk electrode (RDE) were performed at a 5 mV/s scan rate at a rotation speed varying from 650 to 3000 rpm in 0.1 M KOH aqueous solution. The experiments were performed on a three-electrode system with a CNT-modified glassy carbon electrode (GCE) (0.126 cm^2) sealed in Teflon as the working electrode, a platinum foil as the counter electrode, and an Hg/HgO electrode as the reference electrode. Potential values are given vs. RHE. To prepare the catalyst ink, 2.2 μg of modified CNT was were dispersed in 500 μL of deionized water, 5 μL (100-150 $\mu g/cm^2$) of this suspension were spread on the GCE surface using a micro-syringe and allowed to dry in air at room temperature. Electrolytes were saturated with oxygen or inert gas by bubbling O_2 or Ar prior to the start of each experiment.

To determine the electrochemically activated surface (S_{EAS}), amount Q of electricity required to charge the surface of the studied material (C/g) was determined from the CV. In addition, CV without depolarizer (oxygen) in the solution characterized the composition of the active layer on the electrode surface, as manifested by the presence of characteristic peaks.

To determine the activity of the studied materials in ORR, the polarization curves were recorded in O_2 saturated electrolytes. The catalytic activity was determined on the basis of the half-wave potential ($E_{1/2}$, V), the values of the limiting diffusion current density (i_{lim}, A/cm^2), and the current density in the kinetic region, near the steady–state potential (i_{kin}, A/cm^2).

To determine the corrosion resistance of modified CNT, the method of accelerated corrosion testing was used. During tests, the potential was cycled in the range of 0.6–1.3 V (vs. RHE) in 0.1 M KOH at a potential rate of 100 mV/s for 1000 cycles. After 100, 500, and 1000 cycles, changes in Q and activity in ORR were observed.

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CNT modification methods.

Functionalization was carried out using two methods. The first was to treat CNT in 1 M NaOH at 100 ° C for 1 hour. In this case, the effect on the structure of the initial CNT is insignificant and only one type of oxygen-containing groups, i.e., hydroxyl groups, is present on the surface (Binding energy = 533.34 eV), Figure 1a. CNT treated by NaOH are denoted as CNT1. When functionalization is carried out in concentrated HNO_3 at 120°C for 1 hour, strong surface oxidation occurs and several types of oxygen-containing groups are formed (Fig. 1b). In this case, the CNT are denoted as CNT2. Upon decomposition, the O1s XPS spectra of the CNT2 show 3 peaks corresponding to different binding energies, eV: 531.87 (ketone, carbonyl), 533.3 (hydroxyl) and 534.89 (oxygen-containing carboxyl groups) [15, 16].

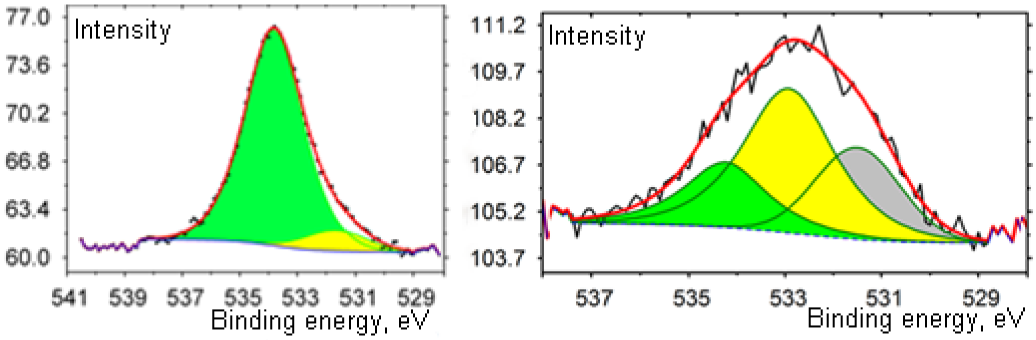

Figure 1. O1s X-ray spectra of CNT functionalized with oxygen-containing groups after treatment: a - NaOH, b - HNO_3.

Nitrogen doping. Functionalized CNT1 or CNT2 was mixed with melamine in a 1: 0.7 ratio and milled in a ball mill for 1 hour at 800 rpm. The resulting mixture was heated at 600°C for 1 hour at an Ar atmosphere. N doped CNT are called CNT (1 or 2) -N.

Phosphorus doping. Functionalized CNT1 or CNT2 were mixed with TPP at a 1: 5 ratio and dissolved in ethanol and sonicated for 30 minutes to form a suspension. The resulting suspension was dried and then heated at 700°C for 1 h in an Ar atmosphere. P–doped CNT are denoted as CNT (1 or 2)-P.

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Dual-doping. To introduce two heteroatoms into the structure of CNT, two doping techniques were combined. First, CNT were doped with nitrogen, then the obtained CNT-N were used as the initial material for doping with phosphorus. The obtained CNT are denoted as CNT (1 or 2) - NP.

Structural Studies. BET surface area and porosity values of the studied materials were determined using the physical sorption method at a Micrometrics ASAP 2020 setup.

The X-ray photoelectron spectra (XPS) were acquired on an Auger spectrometer (Vacuum Generators, UK) with the CLAM2 attachment for measuring XPS spectra. The vacuum in the analyzer chamber was better than 10^{-8} Torr. An Al anode served as the source of monochromatic radiation (200 W). The peak position was standardized based on the position of carbon C1s peak with the energy of 285.0 eV. For quantitative ratios, we used the coefficients of sensitivity shown in the VG1000 program for spectra processing. The surface layer composition was determined to the depth of 10 nm.

3. RESULTS AND DISCUSSION

S_{EAS} values are shown in Table 1. The highest value of Q is achieved after functionalization with acid (CNT2). In this case, the active surface area increases by 3.5 times in comparison with the initial CNT. This is explained by the highest overall oxygen content on their surface (Table 1) among the modified CNT. Furthermore, characteristic peaks at the potential of 0.6 V are observed in the voltammetric curves of CNT2 (Figure 2 (b)), which corresponds to the quinone-hydroquinone conversion [17]. In the XPS spectrum of CNT2, there are binding energy maxima at 531.5–531.9 eV, which can correspond to the C = O groups that are responsible for this conversion [15, 18]. For CNT1 treated with alkali, S_{EAS} increases only by 1.5 times in comparison with the initial CNT, and the overall oxygen content on its surface is 2.18 at.% (Table 1).

Further introduction of P into the structure of CNT results in a decrease in *Q* in the both cases of pre-functionalization (Table 1) and a peak in the anodic region at the potential of E = 1.1 V is observed in the CV (Fig. 2) that is most pronounced on CNT2 - P. Of all the doped CNT, CNT - N have the highest S_{EAS} value, which shows that nitrogen–containing functional groups make a greater contribution to the value of the electrochemically active surface than phosphorus–containing groups. The *Q* values for dual-doped CNT are comparable with the *Q* values for CNT-N. However, the *Q* value for CNT - NP and CNT - N for doped CNT2 is larger than for doped CNT1. The shapes of CV of these materials in the two cases of pre-functionalization are similar

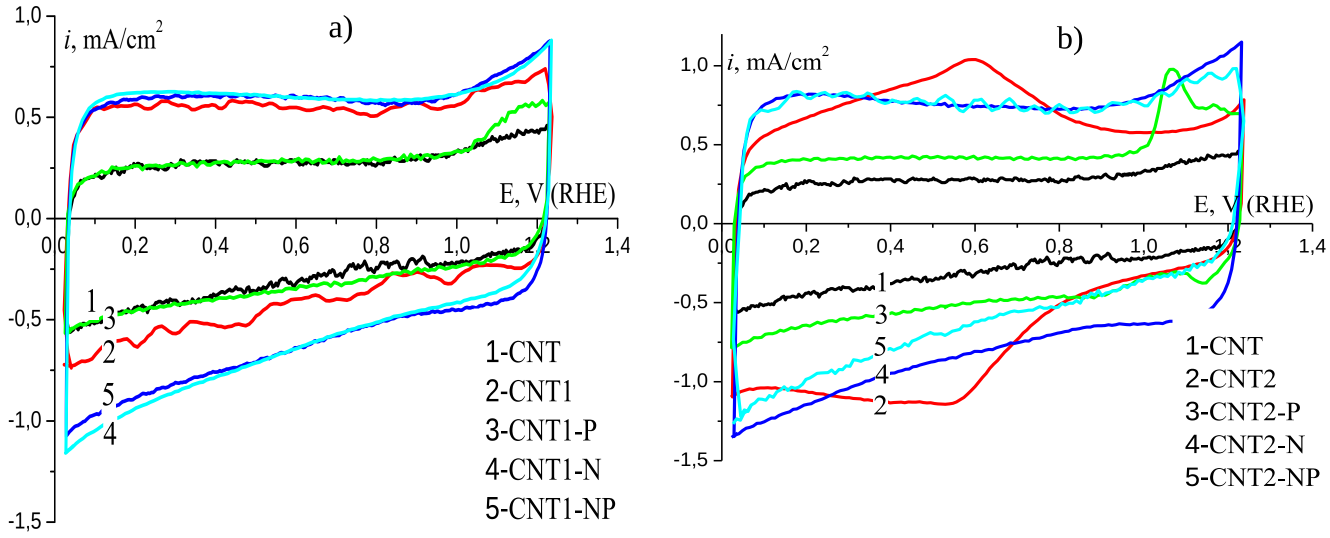

Figure 2. CV on CNT doped by N and P. a – CNT functionalized with NaOH; b – CNT functionalized with HNO_3. Ar -saturated 0.1 M KOH, the potential scan rate is 100 mV/s; m_{cm}=0.15 mg/cm^2.

Also, it should be noted that there is no direct correlation between the content of oxygen-containing groups on the CNT surface and the S_{EAS} value (Table 1). Thus, when the oxygen content on CNT1 is 2.18 at.%, the S_{EAS} value is 75 C/g, while on CNT2 with the oxygen content of 15.4 at.% (7-fold that on CNT1), the electrochemically active surface area is only twice as large (Table 1).

Table 1. Characteristic parameters of CNT after various types of modification.

Nos.	Material	Q, C/g (as S_{EAS})	S_{BET}, m^2/g	$E_{1/2}$, V	i_{kin}, A/cm^2 (E_{st}, V) *	i_{lim}, A/cm^2 at 0.4 V (n)	Element / Overall content, at.%
				1500 об/мин			
1	CNT$_{inital}$	45.5	320	0.64	0.1 (0.750)	2 (1.4)	O/ 0.46
2	CNT 1	75	297	0.66	0.13 (0.750)	2.2 (1.7)	O/2,18
3	CNT 1-P	50	-	0.72	0.6 (0.777)	2.5 (1.8)	O/11,1 N/0,70 P/0.40
4	CNT 1-N	95	269	0.79	1.02 (0.813)	3.62 (2.6)	O/10.08 N/1.15
5	CNT 1-NP	96	172.2	0.79	1.02 (0.819)	3.36 (2.5)	O/ 2.59 N/1.49 P/0.82
6	CNT 2	156	-	0.71	0.23 (0.800)	2.42 (1.8)	O/ 15.4 N/ 1.2
7	CNT 2-P	74	-	0.74	0.49 (0.805)	2.9 (2)	O/ 10.8 N/ 1.0 P/ 0.2
8	CNT 2-N	122	-	0.79	0.92 (0.815)	4.2 (3)	O/12.84 N/1.98
9	CNT 2-NP	108	216.6	0.78	1.19 (0.823)	3.75 (2.7)	O/ 10.8 N/ 1.55 P/ 0.4

* Potential values for the polarization of 0.05 V from the steady–state potential established on modified CNT in an O_2-saturated electrolyte corresponding to i_{kin} values.

The process of CNT1 and CNT2 doping by N and/or P that includes heat treatment (600-700°C) leads to an increase in the amount of oxygen-containing groups on the surface in the case of CNT1 or to its slight decrease for CNT2. Possibly, a certain contribution into the S_{EAS} value is introduced by defects of the porous structure and hydrophilic-hydrophobic properties of the surface that can change in the course of the doping process.

It was previously shown that severe treatment in nitric acid leads to changes in the CNT structure [19]. Shorter fragments of nanotubes are formed and the specific surface decreases, while the amount of oxygen on the surface increases.

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As can be seen in Table 1, a significant amount of oxygen-containing groups is preserved on the surface of all modified CNT2 and the introduction of doping atoms leads only to a slight decrease in the oxygen content, possibly due to replacement of oxygen by nitrogen or phosphorus. In addition, acidic treatment leads to significant structure degradation and to the formation of defects at the ends of nanotubes, which probably can contribute to the S_{EAS} value. This is observed for all CNT2.

To determine the activity in ORR and the effect of the nature and number of functional groups on activity of CNT, polarization curves on RDE were recorded (Figure 3). RDE measurements were carried out in 0.1 M KOH, because ORR catalysis on doped CNT is most pronounced in an alkaline medium and the shape of polarization curves allows as to judge the reaction path. The catalytic effect in ORR can be estimated on the basis of the half-wave potential and the current density at the polarization of 50 mV from the steady–state potential in an O_2-saturated electrolyte. It can be seen that functionalization with oxygen-containing groups causes an $E_{1/2}$ shift in the positive direction and an increase of i_{kin} relative to the initial CNT (Table 1, no. 1 for the initial CNT, no. 2 for CNT1, and no. 6 for CNT2). Here, the more oxygen on the surface, the larger the S_{EAS} value. But the values of $E_{1/2}$ and i_{kin} increase slightly. Subsequent introduction of P atoms into the structure of CNT provides a sharp increase in i_{kin}, 5-fold for CNT1 (Table 1, no. 3) and 2-fold for CNT2 (Table 1, no. 7) and also a positive shift in $E_{1/2}$. The value of i_{kin} indicates that the doping by nitrogen causes an even greater increase in the activity (Table 1, nos. 4, 5 for CNT1 and nos. 8, 9 for CNT2). Thus, CNT-N and dual-doped CNT-NP have the highest activity, irrespective of the method of pre-functionalization and the $E_{1/2}$ value is 0.79 V (vs. RHE). This is 150 mV to the positive of the value for the initial CNT and the i_{kin} value much exceeds that for the initial CNT (Table 1). After co-doping with N and P atoms, no synergistic effect on activity increase is observed. The limiting diffusion current for CNT1-N and CNT2-N is higher than the theoretically calculated value for the two-electron process of oxygen electroreduction (2.8mA/cm^2) ** in an alkaline electrolyte. This indicates the contribution of a 4-electron oxygen reduction reaction on the studied materials. The confirmation of the diffusion nature of the observed limiting current is a linear dependence shown in Fig. 4.

** The values of the diffusion limiting current density are calculated according to the Koutecky-Levich equation [17].

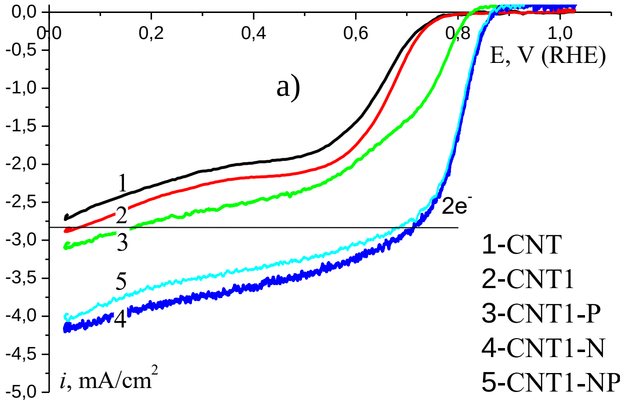

Figure 3. Polarization curves of O_2 reduction on modified CNT functionalized (a) in NaOH and (b) in HNO_3; O_2-saturated 0.1 M KOH, the potential scan rate is 5 mV/s, *w* = 1500 rpm; m_{cm} = 0.15 mg/cm^2.

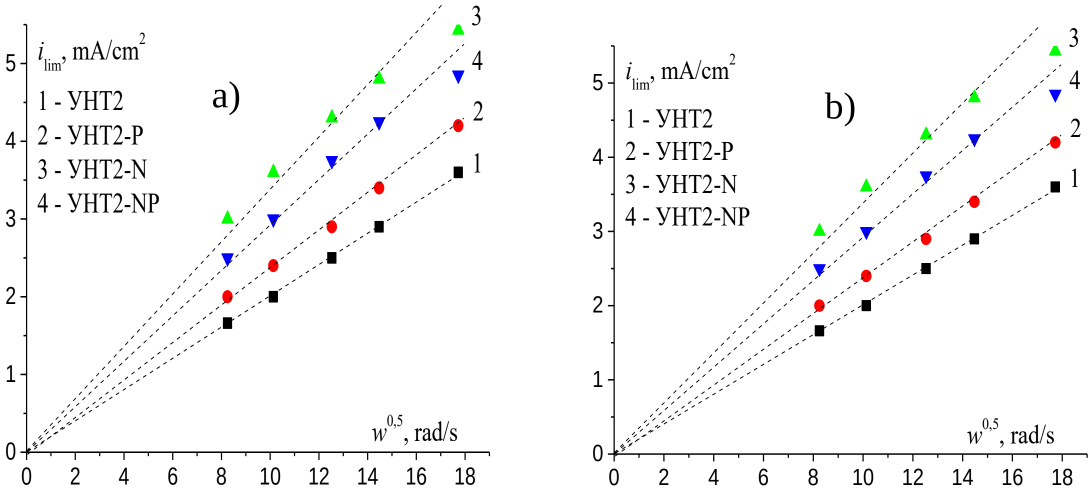

Figure 4. Dependence of i_{lim} on $w^{0.5}$ for modified CNTs functionalized (a) in NaOH and (b) in HNO_3, O_2-saturated 0.1 M KOH, the potential scan rate is 5 mV/s; m = 0.15 mg/cm^2. Each dependence is built on the basis of polarization curves at five electrode rotation speeds (w(rad/s)=68, 103, 157,209, 314).

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The corrosion stability of modified CNT was determined by potential cycling in the range of 0.6–1.3 V (vs. RHE). The cycling was carried out at an Ar atmosphere. Figure 5 shows that all the studied nanotubes are stable under the experimental conditions. The value of the electrochemically active surface area changes slightly in 1000 cycles. However, the maximum surface area decrease of 13% is observed on CNT2 that have the highest S_{EAS}. This is because functionalization in concentrated HNO_3 may cause a change in the porous structure and formation of defects that reduce the stability of CNT during electrochemical corrosion testing. In turn, upon functionalization in NaOH (Figure 5, curve 2), the structure of CNT remains unchanged (Table 1); therefore, CNT1 are characterized by higher stability. However, the values of S_{EAS} and $E_{1/2}$ of nanotubes based on CNT1 are much lower than of those based on CNT2 (Figure 5, curve 7). Figure 5 b) shows the change in the half-wave potential during corrosion testing. The smallest change in the half-wave potential is observed for CNT2 doped by N and N+P.

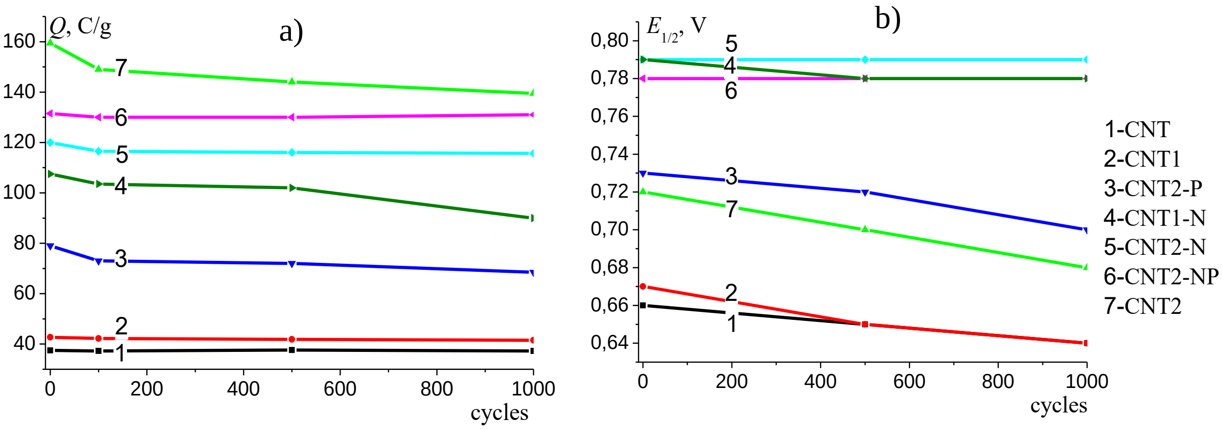

Figure 5. a – Variation of the electrochemically active surface area; b - variation of the half-wave potential during corrosion testing in O_2-saturated 0.1 M KOH, the potential scan rate is 100 mV/s, m_{cm} = 0.15 mg/cm^2.; ΔE = 0.6 ÷ 1.3 V (vs. RHE).

Thus, it can be concluded that high activity in ORR requires a large surface area value provided by functionalization and also the presence of nitrogen and phorphorus that enhance activity and stability. A large electrochemically active surface area observed after CNT functionalization in HNO_3 provides an increase in the ORR currents only due to an increase in the surface area (the current density value in the kinetic range of potentials). Meanwhile, $E_{1/2}$ is practically unchanged at an increase in S_{EAS}. However, the conclusion as to the effect of oxygen–containing groups on the ORR acceleration requires additional studies.

CONCLUSIONS

- Pre-functionalization of CNT with acid or alkali provides an increase in S_{EAS} due to formation of oxygen-containing groups and active centres on the CNT surface. It can be noted that after HNO_3 functionalization, a larger amount of oxygen-containing groups of various types are formed that provide a large contribution into an increase in S_{EAS} and catalytic activity than the hydroxyl groups formed after NaOH functionalization.

- CNT modified by heteroatoms have a high catalytic activity and improved corrosion stability compared to HNO_3–functionalized CNT.

- N- and P-doped CNT can be used as cathode catalysts in alkaline fuel cells, for example, in direct alcohol-oxygen ones. The activity of doped CNT in ORR in alkaline electrolytes approaches that of platinum catalysts. The decrease in overvoltage (half-wave potential) of the ORR reaches 150 mV in comparison with the initial CNT.

- Due to the high catalytic activity, stability and presence of a large amount of active centers on the surface, modified CNT can be used as a substrate for the synthesis of mono- and bimetallic catalysts.

ACKNOWLEDGMENT

This work was carried out with the financial support of the RFBR project BRICS_T No.19-53-80033

CONFLICT OF INTEREST

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The authors declare that they have no conflict of interest

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