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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Catalytic Electroreduction of Oxygen on Products of Pyrolysis of Heterobimetallic Complexes of Zinc

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Abstract—Electrocatalysts for reduction of oxygen were synthesized from AG-3 activated carbon promoted with pyrolized heterobimetallic complexes $[CoLCl_2]$ $[ZnDMFACl_3]$ and $[ML][ZnCl_4]$ (M = Cu^{2+}, Ni^{2+}; L = 4,6,6-trimethyl-1,9-diamino-3,7-diaza-nona-3-ene). The optimal conditions of synthesis of the catalysts, which affect the efficiency of oxygen electroreduction, were found and the activity series of the catalyst in relation to the nature of the second metal was determined.

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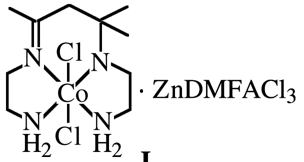
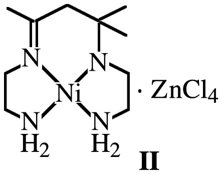
Use of binuclear or heteropolynuclear complexes as precursors in synthesis of reduction electrocatalysts provides better and more stable characteristics in fuel cells and chemical power cells, compared with mononuclear complex compounds [1–3]. The interest in catalysts based on polynuclear complexes is exhibited by scientists in many countries of the world [4]. Catalysts based on mononuclear complexes [5] of phthalocyanine, porphyrin, and some other chelate complexes with *d*-elements are well known, the most active catalysts have been obtained on the basis of cobalt complexes.

Catalysts are commonly synthesized by adsorption of a complex on the support surface, with its subsequent thermal treatment in an inert atmosphere. Pyrolysis in an inert atmosphere of complexes that incorporate ligands coordinated to central atoms via oxygen atoms yields electrocatalysts having active centers in the form of nonstoichiometric metal oxides on the surface of the carbon support [1]. In contrast to spinels, these oxides are more active because they form nanostructures on the support surface, whereas spinels are crystals with poor electrical conductivity [6]. Complexes with ligands coordinated to the central atom via nitrogen atoms enable imitation of pyropolymers produced on the basis of N_4-complexes [7]. They approach in electrical activity the known complexes, but are less expensive in manufacture than porphyrin and phthalocyanine complexes of *d*-elements. Use of heterobimetallic complexes combining different *d*-metals and ligands will make it possible to obtain new high-efficiency electrocatalysts for oxygen reduction and replace some expensive or noble metals. As shown in [3], heteropolynuclear complexes with copper and zinc are good precursors for high-efficiency catalysts, and, therefore, the following heterobimetallic complexes produced by direct template synthesis [8] were used to obtain electrocatalysts for oxygen reduction:



I



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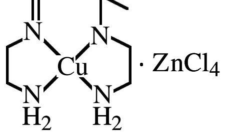

III

where $[CoLCl_2]$ $[ZnDMFACl_3]$ (**I**) and $[ML][ZnCl_4]$ [M = Ni^{2+} (**II**), Cu^{2+} (**III**); L = 4,6,6-trimethyl-1,9-diamino-3,7-diaza-nona-3-ene].

The aim of this study was to examine the influence exerted by the nature of the second metal in heterobimetallic complexes of zinc (Zn^{2+}–M, where M = Cu^{2+}, Ni^{2+}, Co^{2+}) in the reaction of oxygen reduction on

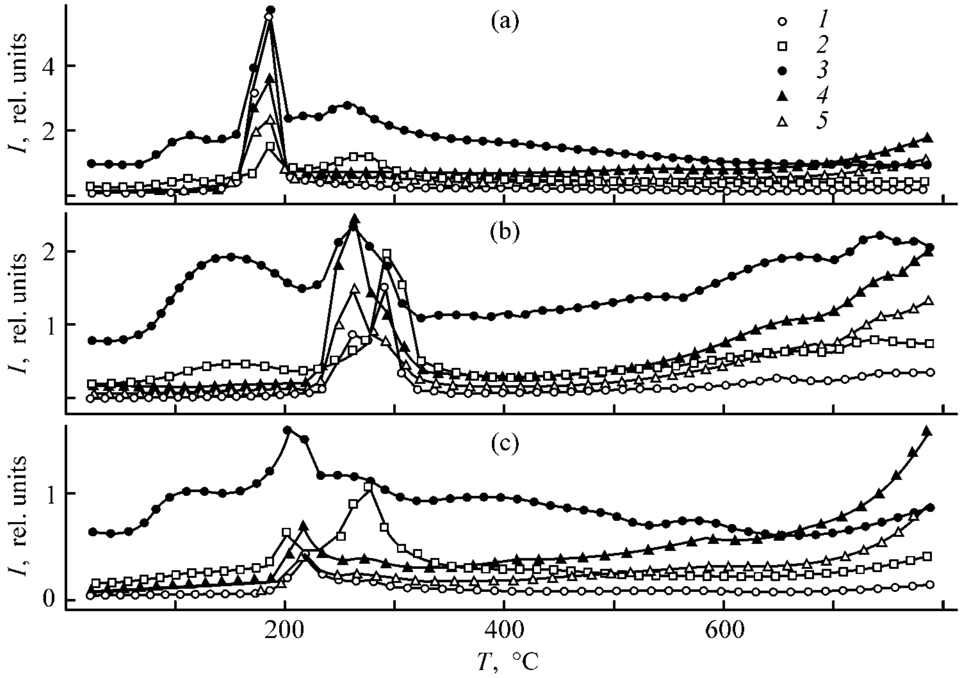

Fig. 1. Thermodesorption mass spectra of the complexes (a) [CoL] [$ZnDMFACl_3$], (b) [NiL][$ZnCl_4$], and (c) [CuL][$ZnCl_4$] in a vacuum at a residual pressure of 10^{-6} Pa and heating rate of 10 deg min^{-1}. (*I*) Ionic current and (*T*) heating temperature. *m*/*z*: (*1*) 15, (*2*) 17, (*3*) 18, (*4*) 28, and (*5*) 29.

the electrocatalytic properties of catalysts produced by the thermal method.

EXPERIMENTAL

To obtain electrocatalysts, heterobimetallic complexes of zinc, **I**–**III**, were synthesized by direct template synthesis [8]. The complexes were dissolved in dimethylformamide and adsorbed on AG-3 high-porosity carbon with a dispersity of less than 50 μm and specific surface area of 850 m^2 g^{-1} (measured by BET). Then, the carbon materials with deposited complex compounds were thermally treated at various temperatures (in the range 200–800°C) in the atmosphere of argon. For this purpose, a 100-mg portion of AG-3 carbon with an adsorbed complex was placed in a tubular quartz furnace through which argon was permanently passed and was gradually heated to a prescribed temperature and kept under these conditions for 1 h. The samples were thermally treated at temperatures of 200, 400, 600, and 800°C and then their catalytic activity in the reaction of oxygen electroreduction was studied.

To determine the composition of products formed in pyrolysis of complexes on the surface of the carbon support, thermal analysis of complexes **I**–**III** was made on a Q-1500D derivatograph (MOM, Hungary). The analysis was performed under the following conditions: weighed portion 500 mg, TG galvanometer sensitivity 500, phase transformations fixed in the range 10–800°C at a heating rate of 5 deg min^{-1} in the atmosphere of argon. Freshly calcined Al_2O_3 served as reference. In a thermal analysis with a large amount of a complex at 180–220°C, the contents of the platinum crucible were ejected because of the pronounced exothermic effect with destruction of the ligand 4,6,6-trimethyl-1,9, diamino-3,7-diaza-nona-3-ene. Therefore, thermal analysis was performed for all the samples in the presence of Al_2O_3 taken in the proportion Al_2O_3 : complex = 0.04 g : 0.16 g. The final products of pyrolysis were analyzed for the content of hydrogen, nitrogen, and carbon, with the result of analysis of the starting complexes taken into account.

The starting complexes were examined by the method of thermal desorption with mass-spectrometric analysis of the species being desorbed on an MX-1302 mass spectrometer under the following conditions: heating temperature 20–800°C, heating rate 10 deg min^{-1} residual pressure 10^{-6} Pa, weighed portion of a complex 1 mg.

The thermal destruction of complex **I** begins with decomposition of dimethylformamide at 50–180°C, which corresponds to loss of 15.1% of the total mass of the complex. In this temperature range, the mass spectrometer records products of pyrolysis, such as NH_4^+, NH_3, CH_3^+. The thermodesorption mass spectra of complex **I** are shown in Fig. 1a. Because the spec-

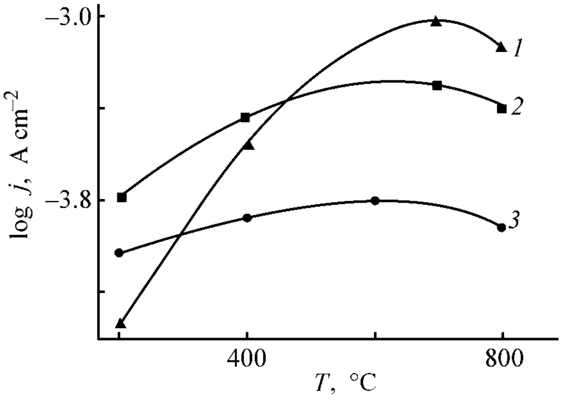

Fig. 2. Rate of oxygen electroreduction on catalysts formed by pyrolysis of heterobimetallic complexes on AG-3 in a 1 M KOH solution at 20°C vs. the pyrolysis temperature *T*. (*j*) Current density. Potential $E = -0.1$ V relative to Ag/AgCl reference electrode. Complex: (*1*) [CuL][ZnCl$_4$], (*2*) [NiL][ZnCl$_4$], and (*3*) [CoL][ZnDMFACl$_3$].

tra are rather intricate, Fig. 1 shows for all the complexes only selected data for species with *m*/*z* less than 29. The mass-spectra clearly show the temperature ranges in which the intensity of pyrolysis of the complexes under study is the highest. At 180–220°C occurs partial decomposition of the ligand (4,6,6-trimethyl-1,9-diamino-3,7-diaza-nona-3-ene) and the thermogravimetric curve demonstrates a considerable loss of mass (12.2%). The mass spectra reveal splitting-off of the following species: NH$_4^+$, NH$_3$, CH$_3^+$, CH–NH$_2^+$, CH–NH$^+$, CH$_2$– CH$_2^+$, etc. Some of the species desorbed add a Cl$^-$ ion to form species with *m*/*z* exceeding 36. Molecular Cl$_2$ formed in pyrolysis may be present in decomposition products in minor amounts, with *m*/*z* of 69, 70, 71. In the following stage of pyrolysis (220–280°C) continues decomposition of the ligand and zinc oxide starts to be formed. In the range 280–620°C occurs full decomposition of the organic ligand to give the final product in the form of a mixture CoCl$_2$ + ZnO, which is confirmed by the results of elemental and thermal analyses.

The thermolysis of complex (**III**) begins with decomposition of 4,6,6-trimethyl-1,9-diamino-3,7-diaza-nona-3-ene. In the temperature range 100–240°C, the mass spectrometer records (Fig. 1c) such desorption products as NH$_4^+$, NH$_3$, CH$_3^+$, CH–NH$_2^+$, CH–NH$^+$, CH$_2$–CH$_2^+$ and chlorine-containing species with heavier mass (loss of mass was 15.1% of the total mass of the complex). At 240–550°C, the decomposition of the organic ligand is complete (37.6%) to give pyrolysis products containing ZnCl$_2$ and fragments of a compound of copper and nitrogen.

Complex (**I**) is more thermally stable. Its destruction also begins with decomposition of the ligand L in the range 130–320°C (15.1%). The decomposition products are similar for complexes **I**–**III** (Fig. 1b). In the range 320–710°C, the decomposition of the ligand L is complete (43.1%) to give pyrolysis products in the form of a mixture Ni + ZnCl$_2$.

The substances obtained were analyzed in the reaction of electrochemical reduction of oxygen in a three-electrode electrochemical cell (with 1 M KOH solution and separated cathode and anode spaces) by the method of the "floating" gas-diffusion electrode [9] at 20°C. The floating gas-diffusion electrode had the form of a pellet of hydrophobized acetylene black containing 30 wt % polytetrafluoroethylene, with a mass of 300 mg, density of 0.95 g cm^{-3}, diameter of 10 mm, and thickness of 2 mm, compacted under a pressure of 5–7 MPa. A nickel-wire current lead was embedded in the pellet. A layer of an electrocatalyst under study, with a particle size of less than 20 μm, was deposited in an amount of 1 mg cm^{-2} onto the electrode surface and compacted under a pressure of 5–6 MPa. This amount of the catalyst provided a kinetic mode of the electrochemical reaction [10]. The catalyst was retained on the surface of the support by adhesion forces. Polarization curves were measured in the potentiostatic mode on a PI-50-1.1 potentiostat with a step of 10 mV. The current was recorded with an M 2020 milliammeter.

The activity was evaluated by the current of oxygen reduction, observed at a potential of –0.10 V, and by the slope of the polarization curve, $\partial E/\partial \log j$ (b_1; b_2). The kinetic characteristics of oxygen electroreduction on the catalyst, obtained in the study, are listed in the table. Dependences of the rate of oxygen electroreduction at a constant potential $E = -0.1$ V on the temperature at which the electrocatalysts based on heterobimetallic complexes were synthesized are shown in Fig. 2. It can be seen from Fig. 2 and the table that the highest current of oxygen reduction is observed for the catalysts obtained from heterobimetallic complexes of copper and zinc at 700°C. It is known that electrocatalysts produced from porphyrin and phthalocyanine complexes [5, 11, 12] at $T \leq 800$°C form active centers in which the MN$_4$ structure is preserved, and its chemical bonding with the carbon support is assumed.

Thus, 700–800°C is the optimal temperature range for production of active catalysts from complexes based on copper–zinc heterobimetallic complexes, which decompose in an inert atmosphere on the carbon surface and, probably, also form metal-and-nitrogen-

Kinetic parameters* of electrocatalytic reduction of oxygen on catalysts formed by pyrolysis of heterobimetallic Zn^{2+}–M complexes (M = Cu^{2+}, Ni^{2+}, Co^{3+}) in 1 M KOH at 20°C

Catalyst	T, °C	E_{st}, V	j_0, A cm^{-2}	$\partial E/\partial \log j$, V	
				b_1	b_2
AG-3	–	–0.094	1.2×10^{-9}	0.045	0.110
Cu–Zn(AG-3)	200	–0.105	5.6×10^{-8}	0.049	0.114
	400	–0.049	3.5×10^{-6}	0.049	0.115
	700	–0.045	7.5×10^{-6}	0.060	0.098
	800	–0.046	4.4×10^{-6}	0.060	0.098
Ni–Zn(AG-3)	200	–0.110	5.7×10^{-7}	0.050	0.117
	400	–0.052	8.1×10^{-7}	0.049	0.108
	700	–0.084	1.4×10^{-6}	0.049	0.115
	800	–0.075	3.2×10^{-7}	0.047	0.118
Co–Zn(AG-3)	200	–0.031	3.2×10^{-7}	0.053	0.116
	400	–0.021	9.5×10^{-7}	0.054	0.116
	700	–0.087	3.0×10^{-6}	0.053	0.115
	800	–0.069	1.0×10^{-6}	0.052	0.117

* j_0, exchange current density; b_1, b_2, slopes of steady-state polarization curves.

containing pyrolysis products bound to the carbon surface. In this case, the most active electrocatalysts for oxygen reduction are formed from Cu–Zn complexes. For catalytic compositions Zn–Co, catalytically active centers are formed at 600°C, as also in the case of oxygen-containing complexes [1–2], which give pyrolysis products in the form of nonstoichiometric oxides. The presence of oxygen in complex **I** contained in dimethylformamide favors formation of various oxide structures on the surface of the carbon support, which provides the electrocatalytic effect of oxygen reduction.

In the case of complex **II**, Ni and $ZnCl_2$, which show weak activity in the reaction of oxygen reduction, are formed in pyrolysis products. The highest current of oxygen reduction at –0.10 V is observed for catalysts synthesized at 700°C from a bimetallic Zn–Cu complex: 1.72 mA cm^{-2} (b_1 = 60 mV, b_2 = 100 mV). Next in activity are the compositions Zn–Co (1.68 mA cm^{-2}, b_1 = 55 mV, b_2 = 115 mV) and Zn–Ni (0.91 mA cm^{-2}, b_1 = 50 mV, b_2 = 110 mV) obtained at 600°C.

The steady-state polarization curves of oxygen reduction on catalysts synthesized at 600°C in the atmosphere of argon are shown in Fig. 3. It can be seen that the change in the steady-state potentials of the catalysts relative to the substrate is approximately 0.10 V. The positive shift of the steady-state polarization curves relative to AG-3 is 0.12 V for catalysts with Zn–Cu, 0.10 V for Zn–Co, and 0.08 V for Zn–Ni; the slopes $\partial E/\partial \log j$ for the catalysts formed on the basis of heterobimetallic complexes are close to those for AG-3 activated carbon. This indicates that the mechanisms of oxygen electroreduction are similar in these cases. The slopes suggest that the electroreduction of oxygen occurs by the single-electron mechanism with slowed-down addition of a first electron and via the stage of formation of hydrogen peroxide, which is characteristic of activated carbons [13]. The kinetic parameters of oxygen electroreduction on catalysts produced from heterobimetallic complexes (see table) show that the highest exchange

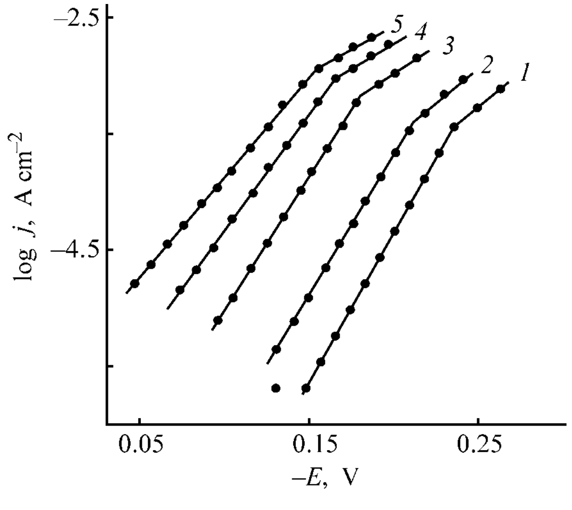

Fig. 3. Potentiostatic polarization curves of oxygen electroreduction, measured on a substrate of hydrophobized carbon black in a 1 M KOH solution at 20°C on catalysts formed by pyrolysis of heterobimetallic complexes on AG-3 at 600°C. (j) Current density and (E) electrode potential. (*1*) Hydrophobized carbon black, (*2*) AG-3 carbon, (*3*) Ni–Zn(AG-3), (*4*) Co–Zn(AG-3), and (*5*) Cu–Zn(AG-3).

currents are observed for the electrocatalyst obtained from the Zn–Cu complex (**III**) at 700°C. Thus, the electrocatalysts prepared from complex (**III**) are more electrically active than (**I**)–(**III**) complexes because their active centers contain a metal and nitrogen bound to surface carbon atoms, as also in the case of pyropolymers [5]. The slopes of the steady-state polarization curves lie within the ranges: $b_1 = 0.04$–0.06 V, $b_2 = 0.10$–0.12 V.

The electrocatalysts obtained can be used in metal-air chemical power cells, fuel cells, and sensors.

CONCLUSIONS

(1) The highest activity is characteristic of catalysts synthesized in thermal destruction of heterobimetallic complexes in the temperature range 500–700°C in the atmosphere of argon.

(2) The catalytic activity of the catalysts for oxygen reduction, prepared on the basis of heterobimetallic complexes of zinc, decreases in the order Zn–Cu > Zn–Co > Zn–Ni.

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