Russian Journal of Applied Chemistry, Vol. 74, No. 7, 2001, pp. 1147–1150. Translated from Zhurnal Prikladnoi Khimii, Vol. 74, No. 7, 2001, pp. 1116–1119.

CATALYSIS

Cobalt(III)–*d*-Metal Triethanolamine Complexes as Catalysts of Electrochemical Reduction of Oxygen

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Received September 12, 2000; in final form, April 2001

Abstract—Carbon-supported oxide catalysts of oxygen electroreduction were prepared from Co(III)–M(II) ethanolamine complexes. The electrochemical properties of these catalysts were studied. The apparent activation energies of the reduction were measured.

Development of new electrocatalysts free from noble metals and electrodes on their base for chemical current sources is an urgent problem [1]. One of the most promising catalysts for oxygen electroreduction in metal–air chemical current sources and electrochemical generators are *d*-metal N_4 complexes [2–5]. Catalysts with required properties can be prepared by variation of the ligands and the central metal. Thermal treatment of carbon materials modified with organometallic N_4 complexes enhances their catalytic activity in electrochemical reduction of oxygen and increases the discharge voltage and capacity of voltaic cells. The structure of catalytically active centers depends on the ligand nature and on the temperature and atmosphere of pyrolysis. For example, the active centers of the catalysts prepared by thermolysis of cobalt(II) and iron(II) polyacrylonitrile complexes at 800–900°C are anchored to the carbon support via nitrogen atoms [2]. When a carbon material modified with products of condensation of ethylenediamine and formaldehyde with *d*-metals are used as the precursors, the most active catalysts are formed at 500–600°C [3]. Effective catalysts of oxygen electrochemical reduction were prepared by heat treatment of polymeric cobalt(III) complexes with *p*-phenylenediamine and 2,6-diaminopyridine at 923–1123°C in a vacuum, with the catalytic activity increasing with the temperature of the heat treatment. Tarasevich and Radyushkina [5] showed that effective catalysts based on cobalt(II) and iron(II) porphyrin and phthalocyanine complexes can be prepared by calcination at 800–900°C. Among the best catalysts are 3*d*-metal oxides with the spinel structure [6]. However, the electrical conductivity of these oxides is low, and preparation of catalysts with high surface conductivity by application of these oxides to carbon support is rather complex problem. The electrocatalytic activity of oxides is known [1, 7] to depend mainly on the nature of surface cations and structural defects. The aim of this work was to prepare catalysts of electrochemical oxygen reduction by pyrolysis of cobalt(III)–*d*-metal(II) triethanolamine complexes on carbon support to form metal oxides with the spinel structure.

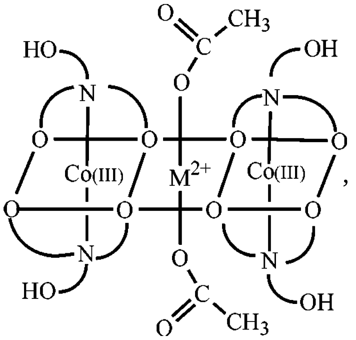
EXPERIMENTAL

Catalysts of electrochemical reduction of oxygen were prepared by treatment of AG-3 activated carbon with methanolic or aqueous-methanolic solutions of $[Co(HTEA)H_2TEA]_2 \cdot M(OOCCH_3)_2$ (where H_3TEA is triethanolamine and M is Mn^{2+}, Ni^{2+}, Cu^{2+}, or Zn^{2+}).

The initial complexes were prepared by addition of a 0.2 M methanolic or aqueous methanolic solution (10 ml) of appropriate *d*-metal (Mn^{2+}, Ni^{2+}, Cu^{2+}, or Zn^{2+}) acetates to 0.004 M methanolic solution (5 ml) of cobalt aminoalcoholate $[Co(HTEA)H_2TEA]_2$ prepared by the procedure in [8]. Methanol was used as the solvent of nickel acetate and zinc acetate and water–methanol mixture (1 : 1), as the solvent for manganese acetate and copper acetate. Manganese(II) acetate was prepared by dissolving metallic manganese in glacial acetic acid, followed by recrystallization from water. The other acetates were of analytically pure grade. AG-3 activated carbon (1 g) with particles smaller than 50 μm and the BET specific surface area of 850 $m^2 g^{-1}$ was added to a solution of appropriate metal acetate. The mixture was allowed to stand for 12 h. Then 80% of the solvent was distilled off. The impregnated carbon was filtered off, washed with a small amount of isopropanol and then with ether, and dried at 120°C to constant weight. The weight gain of the activated carbon after sorption of $[Co(HTEA)H_2TEA]_2 \cdot Mn(OOCCH_3)_2$, $[Co(HTEA)H_2TEA]_2 \cdot Cu(OOCCH_3)_2$, $[Co(HTEA)H_2TEA]_2 \cdot Zn(OOCCH_3)_2$, and $[Co(HTEA)H_2TEA]_2 \cdot Ni(OOCCH_3)_2$ was 51, 55, 20, and 64%, respectively.

The currents passed through the catalysts were adjusted depending on the weight of the complex applied to the carbon.

The triethanolamine complexes have the following structure:



where curve segments denote the $-C_2H_4-$ fragments.

As seen from this figure, the double-charged metal located in the equatorial plane is bound via oxygen bridges to the triple-charged cobalt ions. There are reasons to believe that this fragment in the form of spinel or substoichiometric mixed oxides can be retained on the carbon surface after pyrolysis of the complexes at definite temperatures. Thermal degradation of the complexes of this type in a carbon matrix is known [5] to start from elimination of the terminal groups. The products are incorporated into the structure of the carbon matrix.

A weighed portion of carbon-supported metal complexes (200 mg) was placed in a quartz tube furnace. The sample was gradually heated in an argon counterflow to the required temperature, kept at this temperature for 1 h, and cooled to room temperature. The heat treatment was performed at temperatures from 200 to 800°C with a 100°C increment. The catalytic activity of the resulting samples in electrochemical reduction of oxygen was studied.

The electroreduction of oxygen was performed at room temperature in 1 M KOH on a floating gas-diffusion electrode [11] in an electrochemical cell with separated cathodic and anodic compartments. The electrochemical measurements were performed in a PI-50-1.1 potentiostat using an Ag/AgCl reference electrode. The partial pressure of oxygen before and after bubbling of oxygen through the electrolyte was measured by an OP-210/3 microanalyzer [12].

The working floating gas-diffusion electrode was prepared by the following procedure. A nickel wire was pressed at a pressure of 50–70 kg cm^{-2} in acetylene black (400 mg) hydrophobized with 30% polytetrafluoroethylene. A thin layer of finely divided catalyst (<20 μm) was applied to the surface of the resulting single-layer porous electrode (d = 10.15 mm, density 0.95 g cm^{-3}, thickness ~1 mm). The composite was pressed at 50–60 kg cm^{-2}. The amount of applied catalysts was determined by weighing the electrode before and after pressing of the catalyst powder. To determine the state of the catalyst surface before and after the electrochemical reduction, polarization curves were recorded in an argon atmosphere with a sweeping rate of 2 mV s^{-1}. The potentiostatic polarization curves were constructed from the current densities measured at constant potentials adjusted with a 10 mV increment by a PI-50-1.1 potentiostat. The current was registered with an M-104 milliammeter with extrapolation to $t \to \infty$.

Since the thermal treatment was performed in an inert atmosphere, we suggest that centers active in the oxygen reduction are metal atoms or their oxides dispersed in AG-3 activated carbon. As seen from the kinetic parameters of oxygen electroreduction on the tested catalysts (see table), the active catalysts are formed after calcination of the cobalt triethanolamine complexes on the carbon support at 300–500°C.

The influence of the calcination temperature on the properties of catalysts based on Co(III)–M(II) triethanolamine complexes is seen from the results presented in the table. The maximal exchange currents are observed for the catalysts prepared at 400°C, which is probably due to formation of active centers. With increasing calcination temperature to 800°C, the currents decrease owing to degradation of these centers to form inactive species. The slopes of the stationary polarization curves lie in the following ranges (mV): b_1 = 44–64 and b_2 = 100–127. The dependence of oxygen electroreduction at a constant potential $E = -0.125$ V (vs. silver chloride electrode) on the calcination temperature is shown in Fig. 1. The maximal current was observed with the catalysts calcined at 400°C. This is the best temperature for preparing active catalysts from cobalt(III)–d-metal triethanolamine complexes. The activity of the tested catalysts decreases in the following order: Co–Mn > Co–Zn > Co–Cu > Co–Ni.

The most active catalysts were prepared from Co–Mn triethanolamine complexes. We suggested that

Kinetic parameters of oxygen electroreduction in 1 M KOH at 20°C on catalysts prepared by pyrolysis of the Co(III)–Mn(II) triethanolamine complexes

Catalyst	T, °C	E_{st}, V	$j_0 \times 10^3$, mA cm^{-2}	$\partial E/\partial \log j$, V		W_{app}, kJ mol^{-1}
				b_1	b_2	
AG-3	–	–0.007	11.35	0.058	0.116	60.1
Co–Mn(AG-3)	–	–0.053	4.78	0.061	0.117	56.7
	200	–0.098	5.68	0.046	0.124	56.0
	300	–0.007	5.31	0.049	0.119	55.6
	400	–0.003	12.32	0.064	0.126	54.0
	800	–0.100	4.54	0.048	0.123	59.1
Co–Ni(AG-3)	–	–0.084	2.59	0.052	0.115	60.2
	300	–0.092	1.97	0.056	0.109	59.5
	400	–0.073	2.84	0.048	0.103	58.8
	800	–0.097	1.60	0.060	0.118	60.5
Co–Zn(AG-3)	–	–0.065	5.38	0.060	0.116	60.6
	200	–0.102	3.81	0.057	0.127	60.4
	300	–0.090	4.69	0.055	0.126	59.5
	400	–0.044	10.0	0.047	0.120	59.0
	800	–0.105	3.09	0.054	0.128	60.4
Co–Cu(AG-3)	–	–0.072	3.21	0.047	0.106	60.8
	200	–0.100	1.60	0.047	0.105	60.4
	300	–0.098	1.98	0.044	0.100	60.2
	400	–0.061	2.74	0.046	0.105	59.1
	800	–0.111	0.99	0.046	0.104	60.3

* j_0 is the exchange current density; b_1 and b_2 are the slopes of stationary polarization curves.

the Co–Ni catalysts would be the next in the sequence of the catalytic activity. However, this was not the case. The X-ray diffraction study showed the absence of the crystalline phase. Since the complexes contain oxygen and metal atoms, we suggest that in this case double metal oxides with spinel or nonstoichiometric oxide structure are formed. The catalytically active centers of this catalyst are formed on structural defects [1, 7] containing excess oxygen. The defects promote formation of cationic vacancies and increase the electrical conductivity. As a result, the electrochemical properties of the catalysts are improved.

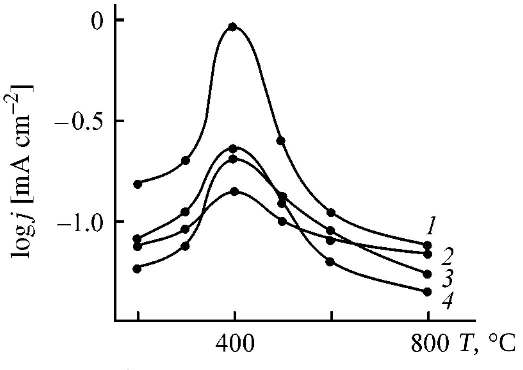


Fig. 1. Rate of oxygen electroreduction in 1 M KOH at 20°C on catalysts prepared by pyrolysis of Co(III)–M(II) triethanolamine complexes on AG-3 activated carbon as a function of the pyrolysis temperature *T*. Potential $E = -0.125$ V vs. silver chloride electrode. (j) Current density. Catalyst: (*1*) Co–Mn, (*2*) Co–Ni, (*3*) Co–Cu, and (*4*) Co–Zn.

These data agree with the results of [13] where spinel and nonstoichiometric oxides prepared also at 300–400°C were used as catalysts.

The ponetiostatic polarization curves of oxygen electroreduction on the catalyst prepared from Co–Mn triethanolamine complexes supported on AG-3 activated carbon, AG-3 activated carbon without supported metal, and hydrophobized carbon black substrate are shown in Fig. 2. As seen from Fig. 2, the activity of the catalysts is higher than that of AG-3 carbon. The stationary polarization curve of the catalysts is shifted by 50 mV to the positive potentials. We also calculated the apparent activation energy of oxygen electroreduction on the catalysts prepared from Co(III)–M(II) triethanolamine complexes supported by AG-3 activated carbon. For this purpose the potentiostatic polarization curves of Co(III)–M(II) electrocatalysts were measured in an oxygen at-

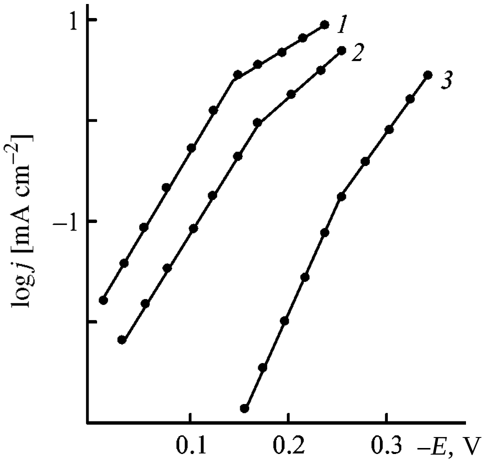


Fig. 2. Potentiostatic polarization curves of oxygen electroreduction measured in 1 M KOH at 20°C on a hydrofibized carbon black substrate. (j) Current density and (E) electrode poetical. (*1*) Co–Mn triethanolamine complex on AG-3 (400°C, Ar), (*2*) AG-3, and (*3*) hydrophibized carbon black.

mosphere at 20, 30, 40, and 50°C to determine the exchange currents. Then the dependences of the exchange currents of oxygen electroreduction on the reciprocal temperature were plotted. The apparent activation energy was calculated by the following equation [14]:

$$W_{\mathrm{app}} = -2.303R\frac{\partial \ln j_0}{\partial (T^{-1})},$$

where W_{app} is the apparent activation energy of oxygen electroreduction, j_0 is the exchange current density, and T is the temperature.

The calculated apparent activation energies of oxygen electroreduction agree with those for the catalysts supported by carbon materials and spinels. The activation energy for the Co–Mn catalysts and AG-3 activated carbon is 54.0 and 60.1 kJ mol^{-1}, respectively. Our results show that the apparent activation energy of oxygen electroreduction decreases with an increase in the catalytic activity. The values of the apparent activation energies and the kinetic data show that the electrochemical reduction is kinetically controlled.

CONCLUSIONS

(1) The best pyrolysis temperature of cobalt–*d*-metal triethanolamine complexes in an inert atmosphere is 300–400°C. Under these conditions the catalysts of oxygen electroreduction were prepared. The spinel and nonstoichiometric oxide structure of the catalysts was suggested.

(2) The most active catalyst was prepared by calcination of Co(III)–Mn(II) triethanolamine complex on AG-3 carbon support at 400°C in an inert atmosphere.

ACKNOWLEDGMENTS

This work was financially supported by the State Foundation for Basic Research of Ukraine.

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