Russian Journal of Applied Chemistry, Vol. 75, No. 2, 2002, pp. 213–218. Translated from Zhurnal Prikladnoi Khimii, Vol. 75, No. 2, 2002, pp. 221–226. Original Russian Text Copyright © 2002 by Nagirnyi, Apostolova, Baskevich, Litvin, Shembel'.

> APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

## Electrolytic Synthesis of Binary Oxide Systems Based on Manganese(II) Oxide

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Received January 15, 2001

Abstract—Joint anodic deposition of manganese, cobalt, nickel, and chromium oxides, which form binary oxide systems, from two-component sulfate solutions of the constituent metals was studied under different electrolysis conditions.

Multicomponent oxide systems of the type  $LiCo_r$ .  $Mn_{2-x}O_4$ , LiCo<sub>v</sub>Mn<sub>2-v</sub>O<sub>4</sub>, and MnV<sub>2</sub>O<sub>5</sub>, prepared by "doping" of traditional electrochemically active oxides of manganese, vanadium, etc., are of interest for developing efficient cathode materials for lithium batteries [1–4]. Such materials are mainly prepared by chemical-thermal synthesis of stoichiometric mechanical mixtures of thermally unstable salts of the corresponding metals (with simultaneous modification of the forming oxide compounds in the presence of lithium carbonate or hydroxide, if necessary). The essential drawback of this method is the difficultly controllable synthesis and the contamination of the final product with impurities formed in side reactions. This makes preferable the electrochemical synthesis of complex oxide systems by anodic deposition from aqueous solutions containing salts of co-deposited metals [5, 6]. The electrolytic synthesis is advantageous because of the possibility of preparing homogeneous materials, whose components, unlike the case of mechanical mixtures, have related structures and can interact at the molecular level. Along with this, the electrochemical method allows fabrication ballastfree cathodes by direct deposition of complex oxide systems onto a smooth or gauze stainless-steel substrate. Vanadium(V) oxide, synthesized simultaneously with manganese oxide, shows better electrochemical performance than the individually synthesized material [7].

Therefore, it was appropriate to study the possibility of preparing complex binary systems by joint electrolytic deposition of oxide compounds of manganese, cobalt, nickel, and chromium from mixed aqueous solutions of salts of metals co-deposited under varied electrolysis conditions. Data of this kind are unavailable in the literature.

The electrolysis was performed in a 0.2-dm<sup>3</sup> temperature-controlled glass cell. Smooth plates of technical grade VT-1 titanium served as a cathode. The oxides under study were deposited as compact coatings on two sides of gauze and plate-like 12X18H9T steel anodes of size  $10 \times 10 \times 0.15$  and  $10 \times 10 \times$ 0.3 mm, respectively, at  $S_a : S_c = 1 : 5$ . An X-ray diffraction analysis was used to study on disperse deposits of weight 0.1-0.15 g, obtained on a smooth VT-1 titanium plate. The solutions were prepared from pure and analytically pure reagents and distilled water. Two-component solutions based on manganese, cobalt, nickel, and chromium sulfates were used in the study. The total concentration of the solutions studied was within the range 0.3-0.4 M at a ratio of the main to doping components from 5:1 to 1:5. All runs were performed at  $85 \pm 3^{\circ}$ C and pH 2.0–2.5. The electrolysis parameters were chosen on the basis of preliminary experimental tests. The deposition rate  $V_{dep}$  (mg cm<sup>-2</sup> h<sup>-1</sup>) was determined from the weight gain upon electrolysis per unit surface per unit time. Polarization curves were taken in a special threechamber cell on a plate-like 12X18H9T steel anode  $(S_a = 1 \text{ cm}^2)$  with surface roughness corresponding to  $\nabla$  7-8 at  $S_a$ :  $C_c = 1$ : 4 and current densities in the range 0.5–50 mA cm<sup>-2</sup>. The potentials were measured relative to a silver chloride reference electrode (E = +0.225 V) with a ShCh-4315 digital voltmeter. The X-ray diffraction analysis was done on a DRON-2 diffractometer. The microstructure of the surface of deposits (1-3.5 µm thick films) was studied with a nanoscope. The quantitative composition

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**Fig. 1.** Deposition rate  $V_{dep}$  of binary oxides vs. the concentration ratio of sulfates of co-deposited metals *C* (M). Total concentration 0.3–0.4 M,  $T = 85^{\circ}$ C, pH 2.0–2.2,  $i_a = 15 \text{ mA cm}^{-2}$ ; the same for Fig. 4. System: (1) Mn–Co, (2) Mn–Ni, and (3) Mn–Cr.

of the deposits was estimated approximately by the oxalate technique chemical analysis [8].

Figure 1 shows how the deposition rate of the systems studied varies with the ratio of the main components in mixed solutions under the indicated conditions of electrolysis. With increasing "dopant" concentration in a solution, the deposition rate gradually decreases in all cases. Comparison of the deposition rates of individual manganese and cobalt oxides from their solutions under comparable conditions of electrolysis (20–25 and 2.5–3.0 mg cm<sup>-2</sup> h<sup>-1</sup>, respectively) shows that the efficiency of the anodic process decreases steadily with increasing dominating role of delayed formation of the "doping phase" in the anodic deposit (Fig. 1, curve 1). Similar dependences were obtained for the systems Mn-Ni and Mn-Cr. However, the deposition rate for these systems decreases more sharply with increasing dopant concentration (Fig. 1, curves 2, 3). This is accounted for by the fact that, under the given conditions, nickel and chromium oxides cannot be deposited directly from their solutions, and are co-deposited with manganese oxide onto the anode. Apparently, the forming manganese oxide acts as a catalyst, energetically facilitating the transition of the conjugate metal ions into the oxide phase and the formation of stable oxide compounds in the joint anodic process.

The feasible anodic reactions corresponding to the systems studied can be represented by equations (1)–(6) [9, 10] and concurrent redox reactions (7), (8):

$$2Mn^{2+} + 3H_2O \rightarrow Mn_2O_3 + 6H^+ + 2e,$$
  
 $E^0 = 1.0 \text{ V},$  (1)

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e,$$
  
 $E^0 = 1.23 V,$  (2)

$$2\text{Co}^{2+} + 3\text{H}_2\text{O} \rightarrow \text{Co}_2\text{O}_3 + 6\text{H}^+ + 2\text{e},$$
  
 $E^0 = 1.8 \text{ V},$  (3)

$$2Ni^{2+} + 3H_2O \rightarrow Ni_2O_3 + 6H^+ + 2e,$$
  
$$E^0 = 1.75 \text{ V}, \qquad (4)$$

Ni<sup>2+</sup> + 2H<sub>2</sub>O → NiO<sub>2</sub> + 4H<sup>+</sup> + 2e,  
$$E^0 = 1.68$$
 V, (5)

$$2Cr^{3+} + 3H_2O \rightarrow 2CrO_3 + 6H^+ + 6e,$$
  
 $E^0 = 1.36 \text{ V},$  (6)

$$Ni_2O_3 + Mn_2O_3 \rightarrow 2NiO + 2MnO_2,$$
 (7)

$$2\operatorname{CrO}_3 + 3\operatorname{Mn}_2\operatorname{O}_3 \rightarrow \operatorname{Cr}_2\operatorname{O}_3 + 6\operatorname{MnO}_2.$$
(8)

Reactions (1)–(6) are related to standard redox systems. The standard electrode potentials for these reactions are given according to the data of [9, 10]. However, only reactions (1)–(3) can actually occur under the conditions considered. In the given case, reactions (4)–(6) are concurrent and can proceed to give oxide compounds only simultaneously with manganese oxidation. Reactions (7) and (8) are quite permissible, with account taken of the probable ionic and interphase interaction of conjugate components in anodic deposition under certain conditions. This is confirmed by X-ray diffraction analysis of the corresponding binary systems, in which the presence of all of the oxide phases described by equations (1)–(4) and (6)– (8) was revealed [reaction (5) is intermediate].

Probably, processes of joint deposition of the oxide systems studied may occur stage by stage or following other, more complex schemes. This is indirectly confirmed by comparative analysis of the  $i_a$ -E dependences characterizing the process of joint deposition (Fig. 2). A characteristic feature of these dependences is the presence of an intermediate plateau at potentials preceding the ascending branch. The relative position and the character of the corresponding curves depend on the manganese to metal salt concentration ratio Mn : M (where M is Co, Ni, and Cr) in solution. It can be seen in Fig. 2 that raising the "dopant" concentration makes the anodic polarization stronger and the current density lower. In this case, the relative shift of the upper portions of polarization curvers for the same binary system at the concentration ratio in solution varied from 3:1 to 1:3 is 0.23-0.25 V,

and that of the lower portions at the level of the inflection points, no more than 0.1 V. At current densities lower than 5 mA cm<sup>-2</sup> the curves virtually merge together, irrespective of the above ratio.

The influence exerted by the nature of a doping component is manifested as enhancement of the anodic polarization in order Co < Ni < Cr, in agreement with the dependences of the deposition rate on the Mn : M ratio in solution (Fig. 1). Comparison of the lower portions of the  $i_a$ -E curves for binary systems with a similar dependence of the anodic deposition of manganese oxide from its solutions shows that oxidation of manganese to give oxide is the potential-determining process, irrespective of the Mn : M ratio. This process is accompanied by simultaneous reactions of binary oxide formation and hydrogen evolution, which are more intensive in the range of the upper ascending branches of the curves.

Probably, the less positive anode potentials in the lower portions of the curves result from the occurrence of reactions of the first stage of magnesium oxidation  $Mn^{2+} \rightarrow Mn^{3+}$  and oxygen discharge on the initial weakly oxidized stainless-steel surface, proceeding with lower energy expenditure. After a solid oxide film is formed on the anode and the limiting diffusion current of the co-deposited metal ions is reached, the process passes into a new stage (upper portions of the curves), with the corresponding change in the relative rates of the concurrent anodic reactions:  $O_2 > oxide(Mn-M)$ . The energy balance of the anodic process as a whole is determined by the polarization of electrode reactions invilving oxygen evolution on the anode surface shielded by a solid oxide film and of co-deposition of oxide compounds of the conjugate oxide system. In this case, raising the concentration of the "doping" phase causes a corresponding increase in the anodic polarization. This follows from a comparison of the upper portions of the curves for the systems with Mn : M ratio higher and lower than unity (Fig. 2, curves 3, 3'; 4, 4'; 5, 5'). As seen, the upper portions of curves 3'-5' lie at more positive potentials than the corresponding portion for deposition of cobalt oxide from its solution.

The current density on the surface preliminarily coated with a solid film of the corresponding binary oxide steadily grows with increasing potential and reaches the limiting values for the given binary system without intermediate plateaus (Fig. 2, curve 5, dashed line). This confirms the considered kinetic origin of the electrode processes studied at different current densities. The last assumption is in accord with the dependences of the deposition rate on the current densities.

aebill 1.0 2.0 E, Vo. cubill E, Vo. **Fig. 2.** Current-voltage characteristics of anodic formation of (1) manganese and (2) cobalt oxides from their solutions and binary oxides from mixed sulfate solutions of co-deposited metals at concentration ratios (3–5) 3 : 1 and (3'-5') 1 : 3. Total concentration 0.3–0.4 M,  $T = 85^{\circ}$ C, pH 2.0. ( $i_a$ ) Current density and (E) potential. System:

70

50

10

 $mA cm^{-2}$ 



(3, 3') Mn-Co, (4, 4') Mn-Ni, and (5, 5') Mn-Cr.

**Fig. 3.** Deposition rate  $V_{dep}$  of the double oxide Mn–Cr vs. anodic current density  $i_a$  at various  $C_{MnSO_4}$ :  $C_{Cr_2(SO_4)_3}$  ratios. Total concentration 0.3–0.4 M,  $T = 85^{\circ}C$ , pH 2.0–2.5.  $C_{MnSO_4}$ :  $C_{Cr_2(SO_4)_3}$ : (1) 5 : 1, (2) 3 : 1, (3) 1 : 1, (4) 1 : 3, and (5) 1 : 5.

sity, observed for the binary systems studied at various Mn : M ratios (for the example of the Mn–Cr system; Fig. 3). The dependences are similar for all Mn : M ratios: the deposition rate sharply increases in a narrow range of current densities and reaches certain limiting values at  $i_a = 15-20$  mA cm<sup>-2</sup>. In this case, the limiting values of  $V_{dep}$  totally coincide with the corresponding values in the dependence of the deposition rate on the Mn : M ratio at constant current density (Fig. 1, curve 3) and decrease at higher "dopant" concentrations.

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 75 No. 2 2002



**Fig. 4.** Diffraction patterns of binary oxides (1) Mn–Ni, (2) Mn–Co, and (3) Mn–Cr, deposited from solutions with concentration ratios  $C_{MnSO_4}$ :  $C_{MSO_4} = 1$ : 3 and heated in air to 420°C for 7 h. ( $I/I_0$ ) Relative intensity and (2 $\theta$ ) Bragg angle.

After the limiting values are reached, the deposition rate gradually decreases with increasing current density, which is due to the growing contribution to the energy balance of the anodic process from the hindered reaction of doping phase formation and to the increasing fraction of joint oxygen evolution. This circumstance is in agreement with the current–voltage characteristics of the anodic formation of the corresponding binary systems (Fig. 2). Apparently, the fraction of the doping phase in the binary deposit must grow in the given case.

Such an increase also takes place when the Mn : M ratio in solution is changed toward increased concentrations of the concurrent component. For example, approximate quantitative estimate of the composition of the binary Mn-Co oxide shows that, with the Mn : Co ratio in solution changed from 1:2 to 1:3, the content of cobalt oxide in the deposit may increase from 12-15 to 20 wt %. For the Mn-Ni and Mn-Cr systems, these values are lower: 10-12 and 5-8 wt %, respectively. Similar relationships are retained for all of the systems studied When the total concentrations of the corresponding components in solution are raised, with other electrolysis conditions being the same. However, at Mn : M < 1 (1 : 2, 1 : 3, etc.) and total concentration above 100 g  $l^{-1}$ , the deposition rate decreases considerably owing to the increased contribution of the hindered formation of the doping phase.

According to the results of X-ray diffraction analysis, the materials studied are two-phase systems consisting of oxide compounds formed by joint deposition on the anode. These compound correspond to the most thermodynamically stable forms: MnO<sub>2</sub>, CoO, Co<sub>3</sub>O<sub>4</sub>, NiO, Ni<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub> (Fig. 4). These systems are the most reliably identified by diffractometry at Mn : M = 3 : 1 and after high-temperature treatment at 400, 650, and 720–750°C. Simultaneous modification of the obtained complex oxides in the presence of lithium hydroxide or carbonate is a prerequisite to synthesis of electrochemically active oxide systems in the form of double spinels of the type LiCo<sub>x</sub>MnO<sub>2-x</sub>O<sub>4</sub>, LiCr<sub>y</sub>MnO<sub>2-y</sub>O<sub>4</sub>, etc.

Presently, the origin of the structural and molecular correlation in the bulk between the systems studied is unclear. A certain information can be obtained from a comparative analysis of the microstructure and microrelief of the surface of thin-film coatings of the corresponding oxides, deposited onto a smooth stainlesssteel substrate at Mn : M = 1 : 2 (Fig. 5).

Analysis of the presented data shows that the structures of individual oxides and mixed oxides differ significantly. For example, photomicrographs of the surface of the deposits, taken under the same magnification, show that the structure of manganese oxide is coarsely grained crystalline with typical layer-by-layer growth of separate grains (Fig. 5a). At the same time, the cobalt oxide structure is more finely grained, with random orientation of crystals (Fig. 5b).

The structure of co-deposited manganese and cobalt oxides in a mixed anodic deposit essentially differs from the structure of the individual oxides in that a peculiar pattern of finely grained randomly distributed "combs" is formed, which makes the specific surface area of the deposits considerably larger (Fig. 5c).

Deposits with a similar structure are also obtained in joint deposition of manganese and nickel oxides. This is possibly due to the similar mechanisms of formation of the double systems under consideration (Fig. 5d), governed by the interaction of conjugate phases in the stage of their formation and crystallization into grains.

Unlike these systems, Mn–Cr oxide is obtained on the anode in the form of finely grained columnar deposit with rather developed surface (Fig. 5e). These deposits are characterized by ordered structure with virtually symmetric alternation of nearly identical valleys and ridges. Apparently, the mechanism of nucleation and interaction of molecules of the conjugate phases is more intensive in this system, compared with deposition of the binary oxides considered in the present study. This impedes growth of manganese



Fig. 5. Photomicrographs of the surface of the electrolytic deposits of (a)  $MnO_2$ , (b)  $Co_2O_3$ , and binary oxides (c) Mn-Co, (d) Mn-Ni, and (e) Mn-Cr obtained from solutions with 1 : 2 concentration ratio of sulfates of co-deposited metals.

oxide crystals and facilitates their degeneration in the early stage of development. These data suggest that, from the standpoint of energetics, the binary oxides studied are a certain in-

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 75 No. 2 2002

termediate system between a homogeneous mechanical mixture and the single-phase chemical compound.

## CONCLUSIONS

(1) It was demonstrated that complex oxide systems, showing promise as active supports for efficient cathodes of lithium batteries, can be obtained in various combinations (Mn–Co, Mn–Ni, Mn–Cr, etc.) by electrolysis of two-component solutions of Mn(II), Co(II), Ni(II), and Cr(III) sulfates at certain ratios of their concentrations and certain electrolysis parameters.

(2) The necessary condition for electrolytic synthesis of such materials is the presence of a base oxide material, which can be deposited individually on the anode in reasonably high yield, e.g., manganese and cobalt oxides.

(3) Of particular interest are binary oxides of the series studied, synthesized from solutions at 2 : 1–1 : 3 concentration ratios of the main to "doping" metal salts at average total concentration of 0.3–0.4 M. The electrolysis parameters are as follows: temperature  $80-85^{\circ}$ C, pH 2.0–2.5, and anodic current density 7.5–25 mA cm<sup>-2</sup>.

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