

Synthesis and Examination of Electrolytic Sodium–Vanadium Oxide Compounds Intended for Cathodes of Lithium Batteries: The Mechanism of Formation of Electrolytic Bronze β - $\text{Na}_x\text{V}_2\text{O}_5$

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Abstract—To determine the mechanism responsible for the formation of electrolytic sodium–vanadium oxide bronze e - $\text{Na}_x\text{V}_2\text{O}_5$, synthesized earlier from acid vanadyl sulfate electrolyte, β -bronze i - $\text{Na}_x\text{V}_2\text{O}_5$ is synthesized by exposing electrolytic oxide e - V_2O_5 in the same sodium-containing electrolyte under open-circuit conditions, with a subsequent annealing of the sample. It is established that the two modifications of β -bronze (e - $\text{Na}_x\text{V}_2\text{O}_5$ and i - $\text{Na}_x\text{V}_2\text{O}_5$) are identical and that electrolytic precursors of β -bronze $\text{Na}_x\text{V}_2\text{O}_5$ form via an ion-exchange mechanism.

INTRODUCTION

Electrolytic sodium–vanadium oxide bronze e - $\text{Na}_x\text{V}_2\text{O}_5$ was synthesized from an acid vanadyl sulfate electrolyte in [1]. Sodium–vanadium oxide bronze β - $\text{Na}_x\text{V}_2\text{O}_5$, where $x = 0.22$ – 0.40 , is usually synthesized for the intercalation cathodes of lithium batteries by a thermal technique [2]. The β - $\text{Na}_x\text{V}_2\text{O}_5$ bronze was also manufactured electrolytically [3–6]. Specific discharge characteristics of electrolytic bronze make it a promising cathode material. Electrolytic bronze was synthesized by electrochemical oxidation of a vanadyl sulfate electrolyte containing sodium ions, with a subsequent high-temperature treatment of the electrolysis product. Sodium ions are incorporated into the deposit in the course of the electrolysis. In doing so, the structure of the vanadium–oxygen cage does not change orthorhombic syngony. The restructuring of the orthorhombic structure into a monoclinic structure of β -bronze occurs during a high-temperature (300 – 500°C) treatment.

In earlier works [1, 3–6], aspects of incorporation of sodium ions into electrolytic deposit e - V_2O_5 were not touched upon. They are dealt with in the present work. Sodium ions are presumably incorporated into a deposit by means of adsorption, mechanical capture, or ion exchange. The last mechanism is presumably the basic one, as follows from information on V_2O_5 as an ion exchanger. Hydrated vanadium pentoxide is viewed as a hydrate of polyvanadic acid $\text{H}_2\text{V}_{12}\text{O}_{31} \cdot n\text{H}_2\text{O}$ [7]. Ions of alkali metals are capable of substituting protons of dodecavanadic acid, yielding products of various degrees of substitution. Products of substitution of dodecavanadic acid protons $\text{M}_x\text{H}_{2-x}\text{V}_{12}\text{O}_{31} \cdot n\text{H}_2\text{O}$ are identical to compounds ($\text{M}/\text{V} < 0.167$) deposited during the acidification of solutions of metavanadates of

alkali metals [8, 9]. The M/V ratio in the substitution products is determined by the ion-exchange coefficient and the ion concentration. For dodecavanadic acid, ions of alkali metals and ion NH_4^+ form a selectivity series $\text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{H}^+ > \text{Li}^+$ [10]. Thus, the proton in dodecavanadic acid is bound to a vanadium–oxygen cage less strongly than the sodium ion. There is evidence that the bond between sodium ions and a vanadium–oxygen cage is of electrostatic nature [11]. Properties of an ion-exchanger are exhibited by gels and xerogels of vanadium pentoxide, and this gives a chance to synthesize β -bronze $\text{Na}_x\text{V}_2\text{O}_5$ using a sol-gel method (SGM) [12]. Manifestation of ion-exchange properties by an electrolytic modification of vanadium pentoxide is presumably feasible as well. In connection with this the hypothesis about ion-exchange properties of e - V_2O_5 we put forth was verified experimentally and confirmed in the present work.

EXPERIMENTAL

Suppose that the ion-exchange mechanism $\text{H}^+(e\text{-}\text{V}_2\text{O}_5)^- \rightarrow \text{M}^+(e\text{-}\text{V}_2\text{O}_5)^-$ is feasible indeed. Then one should expect manifestation of similarity in properties of electrolytic β -bronze $\text{Na}_x\text{V}_2\text{O}_5$ and electrolytic oxide e - V_2O_5 exposed in an acid sodium-containing electrolyte under open-circuit conditions and subsequently annealed. In connection with this, the studies were carried out in the following manner.

“Pure” sodium-free electrolytic oxide e - V_2O_5 was synthesized using the procedure put forth in [13]. Electrolytic β -bronze was manufactured as described earlier in [1]. The electrolysis products were deposited in the

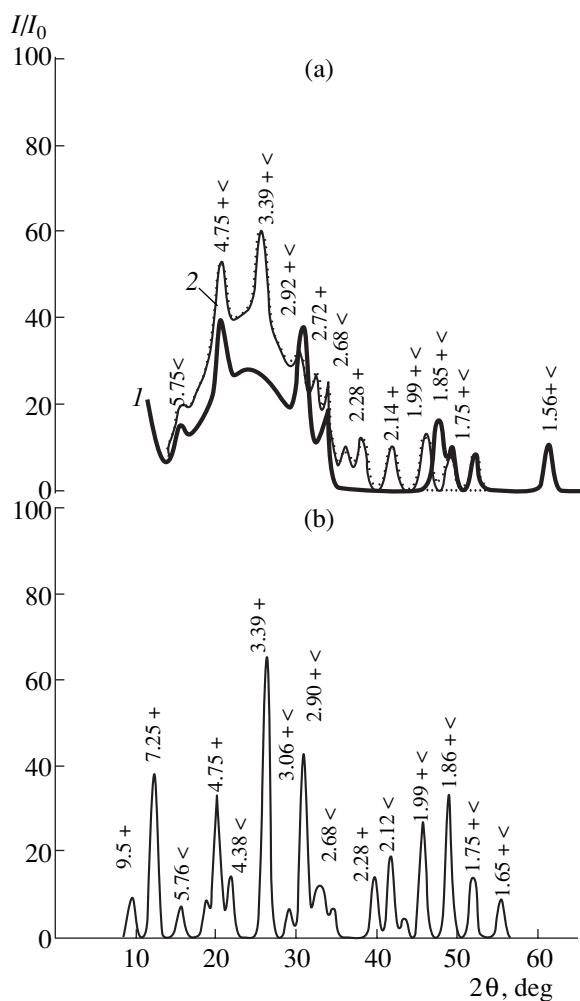


Fig. 1. X-ray diffraction patterns for (a) thermally-nontreated $e\text{-V}_2\text{O}_5$ exposed in 0.2 M VOSO_4 solution of pH 1.8 at 20°C for 15 h (1) in the absence and (2) in the presence of 20 g l^{-1} of Na^+ ions; and (b) $e\text{-V}_2\text{O}_5$ thermally-treated at 500°C for 5 h, exposed for 0.25 h in electrolyte containing 20 g l^{-1} of Na^+ ions; signs “+” and “v” refer to reflexes of bronze and $e\text{-V}_2\text{O}_5$; CuK_α radiation.

form of powder and also in the form of a compact formation on an electroconducting substrate (steel 18Kh12N10T). In the last case, a ballast-free cathode for a lithium battery formed, which contained no binder or electroconducting additive of composite electrodes. Sodium-free samples (200 mg $e\text{-V}_2\text{O}_5$ powder or ballast-free cathode of $e\text{-V}_2\text{O}_5$) were exposed in a sodium-containing electrolyte (50 cm^3) containing 0.2 M VOSO_4 and Na_2SO_4 (20 g l^{-1} Na^+), of pH 1.8, under open-circuit conditions. A sodium-containing electrolyte of this particular composition is used when synthesizing electrolytic bronze $\beta\text{-Na}_x\text{V}_2\text{O}_5$ [1]. The electrolyte temperature was maintained equal to 85–90°C. Once the samples were removed from electrolyte, they were washed with distilled water acidified to pH 1.8 with sulfuric acid. The washed samples were dried in an exsiccator at a temperature of 18–20°C for 24 h over a

layer of P_2O_5 or annealed at a temperature of 300–500°C for 5–7 h. Subsequently, an attempt was made to find similarity between characteristics of synthesized electrolytic β -bronze and samples of $e\text{-V}_2\text{O}_5$ exposed in a sodium-containing electrolyte under open-circuit conditions.

The bronze thus manufactured was characterized by methods of thermal analysis, absorption IR spectroscopy, and X-ray diffractometry described in [1]. Micrographs of powders of vanadium-oxide compounds (VOC) under study were made with the aid of a JEOL JSM-840 scanning electron microscope. The sodium/vanadium ratio in a bronze was determined by means of an elemental analysis. The electrochemical studies were carried out on ballast-free electrodes with an active-component weight of 1.7–2.0 mg cm^{-2} and composite electrodes with an active-component weight of 10–20 mg cm^{-2} in lithium battery models with electrolyte containing propylene carbonate (PC), dimethoxyethane (DME), and 1 M LiClO_4 [1].

The ion-exchange properties of crystalline vanadium pentoxide $c\text{-V}_2\text{O}_5$, manufactured in the Ural plant of chemical reactants, were studied as well. According to X-ray diffractometry data, the size of crystallites of $c\text{-V}_2\text{O}_5$ was $L = 33.9\text{--}36.7$ nm.

EXPERIMENTAL DATA

X-Ray Diffraction Analysis

Specific features of the electrolytic vanadium oxide compounds ($e\text{-VOC}$), as revealed by X-ray diffractometry, are dependent on the mode of their thermal treatment. Structures of thermally treated and nontreated $e\text{-VOC}$ differ. Nontreated $e\text{-VOC}$ have the structure of orthorhombic vanadium pentoxide. X-ray diffraction patterns for nontreated samples of $e\text{-V}_2\text{O}_5$, which were exposed in electrolytes with and without sodium ions under open-circuit conditions, are presented in Fig. 1a. The patterns feature wide halos and low-intensity reflexes. The patterns for samples exposed in electrolytes with and without sodium exhibit reflexes produced by V_2O_5 and $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ oxides. At the same time, the patterns for samples exposed in a sodium-containing electrolyte have additional lines of diffraction reflection intrinsic to $\beta\text{-Na}_x\text{V}_2\text{O}_5$ bronze; these are marked in Fig. 1 with the plus sign. With the time of the $e\text{-V}_2\text{O}_5$ exposure in electrolyte increased, the intensity of reflexes drops, which correlates with a decrease in the size L of the oxide compound crystallites caused by its dissolution in an acid environment. It is established that, depending on the exposure time, L takes on different values in the interval 76–13 nm. The degree of crystallinity of exposed $e\text{-V}_2\text{O}_5$ samples decreases with increasing exposure duration.

A comparison of X-ray diffractometry data for thermally-nontreated $e\text{-V}_2\text{O}_5$ samples, which were exposed in a sodium-containing electrolyte under open-circuit conditions, with those obtained earlier for thermally-

nontreated precursors of electrolytic bronze $e\text{-Na}_x\text{V}_2\text{O}_5$ [5, 6] reveals their similarity. The similarity consists in that in either case X-ray diffraction patterns display diffraction reflection lines of V_2O_5 . At the same time, X-ray diffraction patterns for samples of thermally-nontreated electrolytic deposits manufactured in a sodium-containing electrolyte with a current on display additional reflexes in the region of reflection angles $\theta = 12.4$ degrees ($d = 0.359$ nm) and $\theta = 14.9$ degrees ($d = 0.299$ nm) in the CuK_α radiation.

Annealed $e\text{-VOC}$ alter their structure, which follows from their X-ray diffraction patterns (Fig. 1b): the patterns have no wide halos or smeared reflexes, the reflex intensity increases and their position alters, as compared with non-annealed $e\text{-VOC}$ samples. During the annealing of samples produced in the presence of sodium ions with and without the current, a compound with the structure of monoclinic β -bronze $\text{Na}_x\text{V}_2\text{O}_5$ forms. This follows from practically identical positions of reflexes in the X-ray diffraction patterns for electrolytic bronze (Fig. 2a) and the annealed compound formed during the $e\text{-V}_2\text{O}_5$ exposure in a sodium-containing electrolyte under open-circuit conditions (Fig. 2b). The patterns differ in the reflex intensities. The intensity of reflexes produced by electrolytic bronze is higher than that produced without current, which is explained by different size of crystallites of samples under comparison. Crystal lattice parameters determined for electrolytic bronze and bronze produced without current ($i\text{-Na}_x\text{V}_2\text{O}_5$) are presented in Table 1 and compared with the data for thermal bronze $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$.

The yield of electrolytic bronze depends on the balance between rates of anodic formation and chemical dissolution of $e\text{-V}_2\text{O}_5$ and the rate of incorporation of sodium ions into this oxide. Some information about the kinetics of currentless incorporation of sodium ions into the $e\text{-V}_2\text{O}_5$ oxide were obtained by means of an X-ray analysis of the final product of the synthesis as a function of exposure of $e\text{-V}_2\text{O}_5$ in a sodium-containing electrolyte. In the course of exposure 15 to 24 h long, ionic equilibrium H^+/Na^+ is established; as a result, the annealing of sodium-containing $e\text{-V}_2\text{O}_5$ yields a single-phase product, specifically, $\beta\text{-Na}_x\text{V}_2\text{O}_5$. At shorter exposures (0.15–3 h), the synthesis product contains, in addition to monoclinic bronze, orthorhombic vanadium pentoxide (Fig. 2b).

The incorporation of sodium ions into the $e\text{-V}_2\text{O}_5$ oxide is a rather fast process. According to an X-ray diffractometry analysis, approximately 85% of incorporated sodium ions are incorporated in the oxide within 0.25 h, and then the incorporation process slows down.

An important feature common for the electrolytic synthesis and the synthesis under open-circuit conditions is the formation, in the final analysis, of monoclinic bronze $\beta\text{-Na}_x\text{V}_2\text{O}_5$, when electrolytic vanadium pentoxide in an acid medium is surrounded by sodium ions. The results we presented demonstrate that

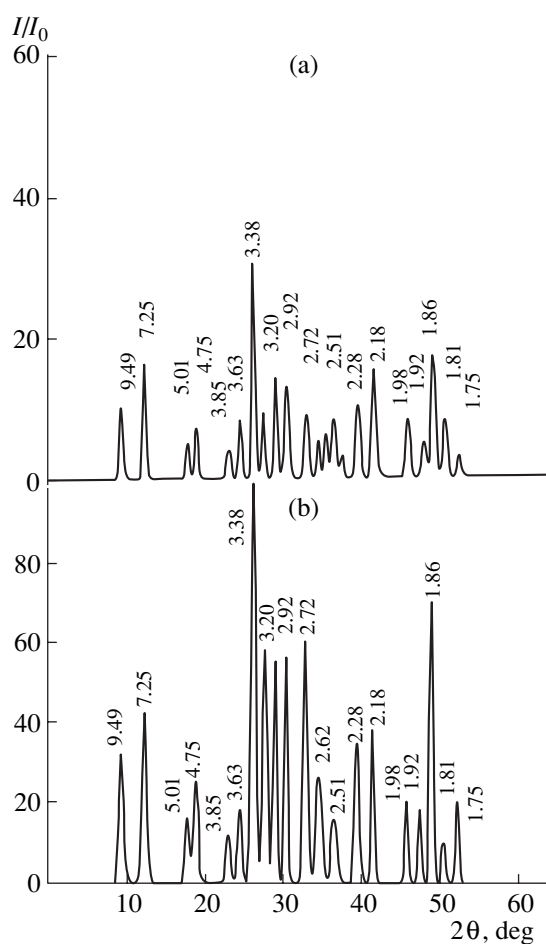


Fig. 2. X-ray diffraction patterns for (a) $e\text{-Na}_x\text{V}_2\text{O}_5$ bronze and (b) $e\text{-V}_2\text{O}_5$ oxide kept for 24 h in Na^+ -containing electrolyte and annealed at 300°C for 5 h; CuK_α radiation.

β -bronze $\text{Na}_x\text{V}_2\text{O}_5$ may be synthesized by an ion-exchange technique, using electrolytic modification $e\text{-V}_2\text{O}_5$ in contact with sodium ions in an acid medium. Experimental data testify to ion-exchange properties of electrolytic modification of vanadium pentoxide.

A check-up on the ion-exchange properties of the crystalline modification, $c\text{-V}_2\text{O}_5$, showed the following. X-ray diffraction patterns for the initial $c\text{-V}_2\text{O}_5$ and for $c\text{-V}_2\text{O}_5$ exposed in a sodium-containing electrolyte with subsequent annealing do not differ in the position

Table 1. Crystal lattice parameters for three β -bronze modifications $\text{Na}_x\text{V}_2\text{O}_5$

| Technique for β -bronze production | Lattice parameter | | | | References |
|--|-------------------|----------|----------|----------------|------------|
| | a , nm | b , nm | c , nm | β , grad | |
| Under current | 1.0078 | 0.3612 | 1.5435 | 109.60 | [1] |
| Currentless | 1.0092 | 0.3609 | 1.5371 | 109.53 | This work |
| Thermal | 1.0080 | 0.3610 | 1.5440 | 109.40 | [2] |

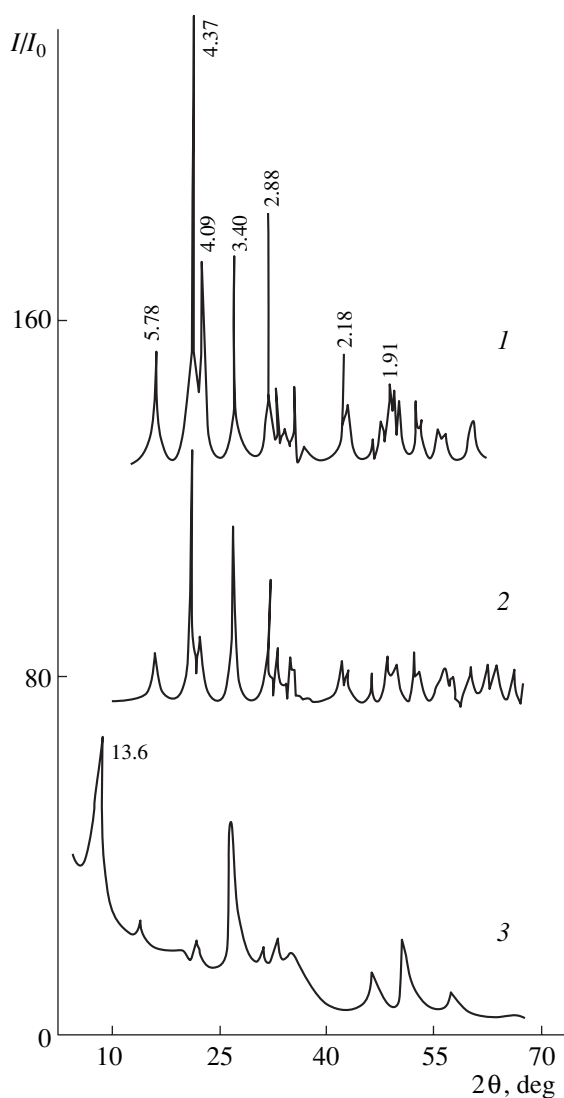


Fig. 3. X-ray diffraction patterns for (1) $c\text{-V}_2\text{O}_5$, (2) $c\text{-V}_2\text{O}_5$ kept for 24 h in 0.2 M VOSO_4 solution containing 20 g l^{-1} of Na^+ ions and annealed at 500°C for 5 h, and (3) $e\text{-V}_2\text{O}_5$ dried in air at 20°C ; $\text{CuK}\alpha$ radiation.

of reflexes (Fig. 3). They differ in their intensity, which is determined by the size of crystallites L . The magnitude of L for exposed $c\text{-V}_2\text{O}_5$ decreases in an acid medium due to dissolution. One visually observes a change in the color from yellow–brown to gray in surface layers of the $c\text{-V}_2\text{O}_5$ oxide annealed after its exposure in a sodium-containing electrolyte. In the deeply situated layers of oxide particles, the color does not alter. This is seen upon grinding the oxide powder. Bronze $\beta\text{-Na}_x\text{V}_2\text{O}_5$ is black, with hues of brown and gray. Judging by these observations, ionic exchange occurs at the surface of $c\text{-V}_2\text{O}_5$ and does not involve deep layers of crystallites.

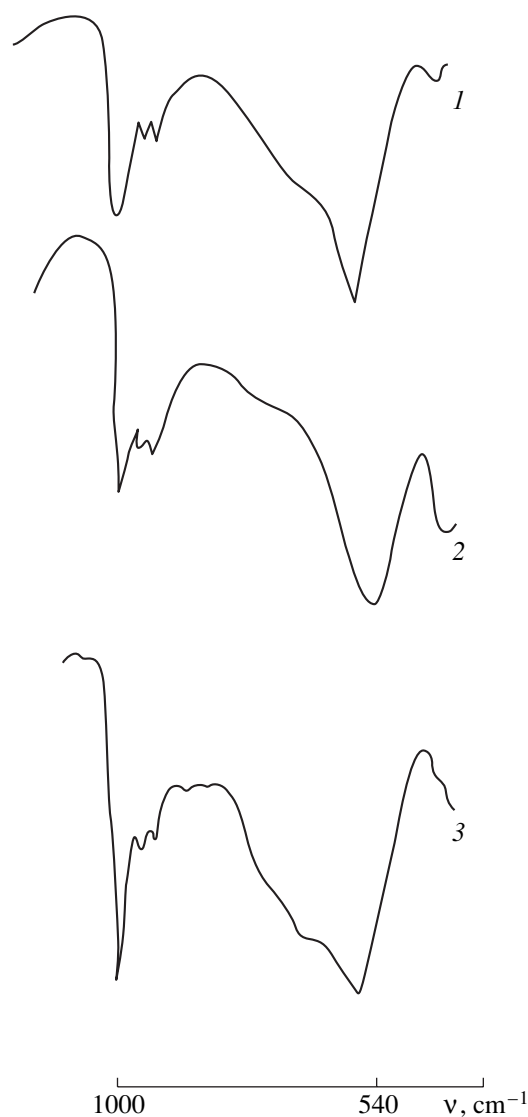


Fig. 4. IR absorption spectra for $\beta\text{-Na}_x\text{V}_2\text{O}_5$ manufactured by (1) thermal, (2) electrolytic, and (3) ion-exchange techniques.

Absorption IR Spectroscopy

As we demonstrated in the previous section, according to the X-ray diffractometry data, electrolytic bronze $\beta\text{-Na}_x\text{V}_2\text{O}_5$ and that manufactured under open-circuit conditions are identical. However, the X-ray diffractometry method fails to give any information about local restructuring processes occurring in the bronze. To obtain such information, we used in this work the absorption IR spectroscopy method [14]. The absorption IR spectra for bronze $\beta\text{-Na}_x\text{V}_2\text{O}_5$ manufactured by thermal, electrolytic, and ion-exchange techniques are presented in Fig. 4. The similarity between these spectra follows from the characteristic absorption bands with maximums near wave numbers 1000 and 560 cm^{-1} .

Thermoanalytical Investigation of β - $\text{Na}_x\text{V}_2\text{O}_5$

Comparing derivatograms for electrolytic bronze produced under open-circuit conditions and for thermal bronze shows their identical behavior during a thermal treatment. The heating curves (TG, DTG, DTA) for thermally-nontreated *i*-bronze manufactured from electrolytic vanadium pentoxide kept in a sodium-containing electrolyte under open-circuit conditions are presented in Fig. 5. The heating results in a weight loss with a maximum rate occurring at 60–180°C. The overall weight loss during the heating up to 400°C is 1.5 M $\text{H}_2\text{O}/1 \text{ M } \text{V}_2\text{O}_5$. The weight loss is accompanied by the heat absorption (endoeffect I, 140°C). At 390°C, a discernible exoeffect occurs. In a high-temperature region, a more considerable endoeffect (II) with two maximums at 630 and 665–675°C is accompanied by a gain in weight. A DTA curve during cooling displays exoeffect (570°C). A derivatogram for annealed *i*-bronze (Fig. 5, dashed line) is characterized by endoeffect (II) in a high-temperature region (630 and 675°C) and exoeffect (610°C) during cooling.

In previous work [1], derivatograms for thermal and electrolytic bronzes were analyzed and the nature of thermal effects was described with allowance made for the literature data. A derivatogram for *i*-bronze is similar to derivatograms for thermal and electrolytic bronzes. Results of a thermal analysis of three bronze modifications, which appear in Table 2, convincingly demonstrate that the properties displayed by the bronze modifications under study converge.

Micrographs of Powdered VOC

The morphology of electrolytic VOC depends on the thermal treatment conditions. Deposits of thermally-nontreated sodium-containing and sodium-free VOC samples and VOC samples annealed at temperatures below the crystallization point (below 300°C) have practically identical morphology (Fig. 6, frames 1, 3, 4, 6). The surface of all these samples is well developed and has blisters, protrudings, and convolutions. It is characterized by the absence of individual structural units. As a result of crystallization upon a high-temperature action (500°C), the structure of deposits becomes ordered: one can see individual structural formations in

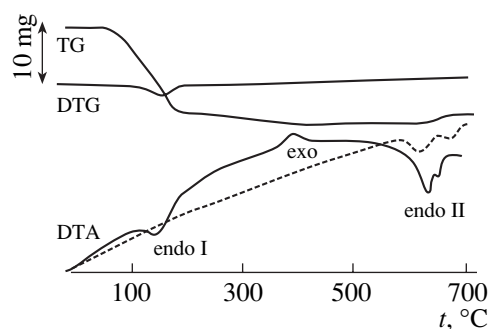


Fig. 5. Derivatogram for thermally-nontreated *e*- V_2O_5 exposed for 24 h in Na^+ -containing electrolyte under open-circuit conditions; dashed line represents DTA curve for *e*- V_2O_5 thermally-treated at 500°C for 5 h and exposed for 24 h in Na^+ -containing electrolyte under open-circuit conditions.

the micrographs. Dimension of formations for electrolytic bronze is 0.5 by 0.5–4.0 μm (Fig. 6, frame 2) and that of electrolytic vanadium pentoxide reaches 1.0 μm (Fig. 6, frame 5). Crystalline *e*- V_2O_5 (Fig. 6, frame 5) differs from crystalline *c*- V_2O_5 produced by the Ural plant of chemical reactants (Fig. 6, frame 7). The morphology of the latter is represented by smooth plates limited by dimensions 1.0 by 0.5 by 0.2–0.5 μm . After exposure in an acid medium (pH 1.8), the plates diminish in size and become rounded (Fig. 6, frame 8).

Elemental Analysis of Bronze

According to the elemental analysis data, electrolytic bronze corresponds to the composition $\text{Na}_{0.22}\text{V}_2\text{O}_5$, and that manufactured by an ion-exchange method on the basis of electrolytic vanadium pentoxide has the composition $\text{Na}_{0.26}\text{V}_2\text{O}_5$. The composition of either bronze modification lies in the region of homogeneity of β -bronze with $x = 0.22$ –0.40.

Specific Surface Area of Bronze

The specific surface area of electrolytic bronze in the case of thermally-nontreated samples of powder, as determined by the BET method (1.33 $\text{m}^2 \text{g}^{-1}$) is more

Table 2. Result of thermal analysis for three bronze modifications

| Bronze sample | Temperature (°C) of endo- and exothermal effects | | | | |
|---|--|---------|-----|---------|-----|
| | Heating | | | Cooling | |
| | Endo I | Endo II | | Exo | |
| <i>e</i> - $\text{Na}_x\text{V}_2\text{O}_5$ (Thermally-nontreatment) | 140 | 627 | 655 | 390 | 575 |
| <i>i</i> - $\text{Na}_x\text{V}_2\text{O}_5$ (Thermally-nontreatment) | 140 | 625 | 665 | 410 | 570 |
| $\text{Na}_{0.33}\text{V}_2\text{O}_5$ (Thermal) | | 635 | 690 | | 595 |
| <i>i</i> - $\text{Na}_x\text{V}_2\text{O}_5$ (Thermally-treatment) | | 630 | 675 | | 610 |

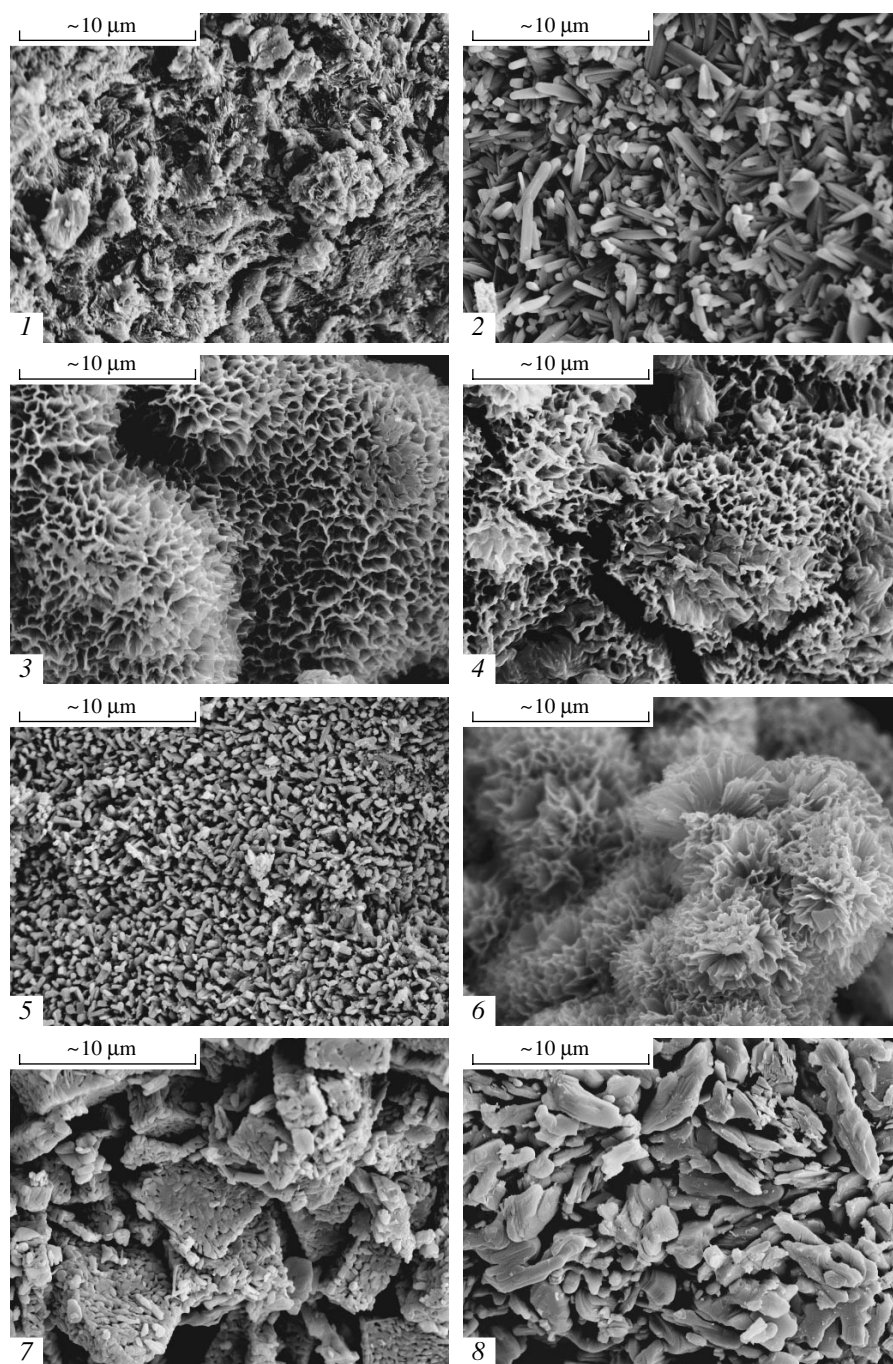


Fig. 6. Micrographs of powders of VOC synthesized at different temperatures: (1) $e\text{-Na}_x\text{V}_2\text{O}_5$ at 20°C, (2) $e\text{-Na}_x\text{V}_2\text{O}_5$ at 500°C, (3) $e\text{-V}_2\text{O}_5$ at 20°C, (4) $e\text{-V}_2\text{O}_5$ at 300°C, (5) $e\text{-V}_2\text{O}_5$ at 500°C, (6) $i\text{-Na}_x\text{V}_2\text{O}_5$ at 120°C, (7) $c\text{-V}_2\text{O}_5$, and (8) $c\text{-V}_2\text{O}_5$ kept for 24 h in Na^+ -containing electrolyte and annealed at 500°C for 5 h.

than 1.5 times that of samples annealed at 500°C ($0.77 \text{ m}^2 \text{ g}^{-1}$).

Electrochemical Characteristics of Intercalation Cathodes Based on β -Bronze $\text{Na}_x\text{V}_2\text{O}_5$

The open-circuit voltage (OCV) of i -bronze and e -bronze in an electrolyte containing PC, DME, and 1 M

LiClO_4 is 3.60 V, which is somewhat lower than OCV of “pure” electrolytic vanadium pentoxide (3.70 V). Galvanostatic discharge curves of β -bronze modifications under study were analyzed in ballast-free and composite electrodes. In thin-layered ballast-free electrodes, electrochemical characteristics of samples of oxide $e\text{-V}_2\text{O}_5$, bronze $e\text{-Na}_x\text{V}_2\text{O}_5$, and bronze $i\text{-Na}_x\text{V}_2\text{O}_5$ are compared.

Discharge curves for ballast-free cathodes based on VOC are presented in Fig. 7a. The voltage dependence of the discharge capacity of oxide $e\text{-V}_2\text{O}_5$ is monotonic function (curve 1). The dependence differs from those for the electrolytic bronze and the bronze manufactured under open-circuit conditions in that there are no horizontal plateaus of voltage. The discharge curve for electrolytic bronze (curve 2) exhibits three horizontal-sloped plateaus of voltage, namely, 3.40–3.30, 2.95–2.90, and 2.60–2.55 V. The discharge curve for the bronze manufactured under open-circuit conditions (curve 3) is characterized by the presence of two horizontal plateaus of voltage, specifically, near 2.90 and 2.60 V, and a shorter plateau at 3.40–3.30 V which is absent sometimes. The specific discharge capacity of bronze modifications under comparison is 200–220 A h kg⁻¹ when discharged at a current density of 50 $\mu\text{A cm}^{-2}$ to a voltage of 2.40 V. There is certain similarity in electrochemical characteristics of bronze modifications under study, namely, the equality of OCV and the presence of plateaus of voltage during the discharge near 2.90 and 2.60 V. The absence of a short plateau of voltage at 3.40–3.30 V in the discharge curve for the bronze manufactured under open-circuit conditions may be connected with different exposure of samples under comparison in a sodium-containing electrolyte and, as a result, different degree of substitution H^+/Na^+ .

Electrochemical characteristics of the electrolytic bronze and the bronze manufactured under open-circuit conditions in composite electrodes confirmed the obtained data for ballast-free cathodes. This follows from the discharge curves presented in Fig. 7b.

Investigation of Ion-Exchange Properties of Crystalline Modification $c\text{-V}_2\text{O}_5$

The discharge curves for a composite electrode based on crystalline vanadium pentoxide $c\text{-V}_2\text{O}_5$ barely differ from those for the $c\text{-V}_2\text{O}_5$ oxide exposed in a sodium-containing electrolyte (Fig. 7c). Under the action of sodium ions, the discharge curve for $c\text{-V}_2\text{O}_5$ turns more monotonic in the voltage region 3.20 to 3.00 V, and an additional inflection in the curve appears near 2.60 V.

DISCUSSION

In this work, using various instruments and methods, we established that two bronze modifications are identical. One modification is electrolytic bronze $e\text{-Na}_x\text{V}_2\text{O}_5$. The other is bronze $i\text{-Na}_x\text{V}_2\text{O}_5$, synthesized under open-circuit conditions during exposure in a sodium-containing solution of oxide $e\text{-V}_2\text{O}_5$ with its subsequent annealing. Electrolysis intermediates only a means for manufacturing oxide $e\text{-V}_2\text{O}_5$ protonated in an acid medium and capable of undergoing the replacement $\text{H}^+ \rightarrow \text{Na}^+$. In the case of the synthesis of electrolytic bronze, ionic exchange $\text{H}^+ \rightarrow \text{Na}^+$ occurs in

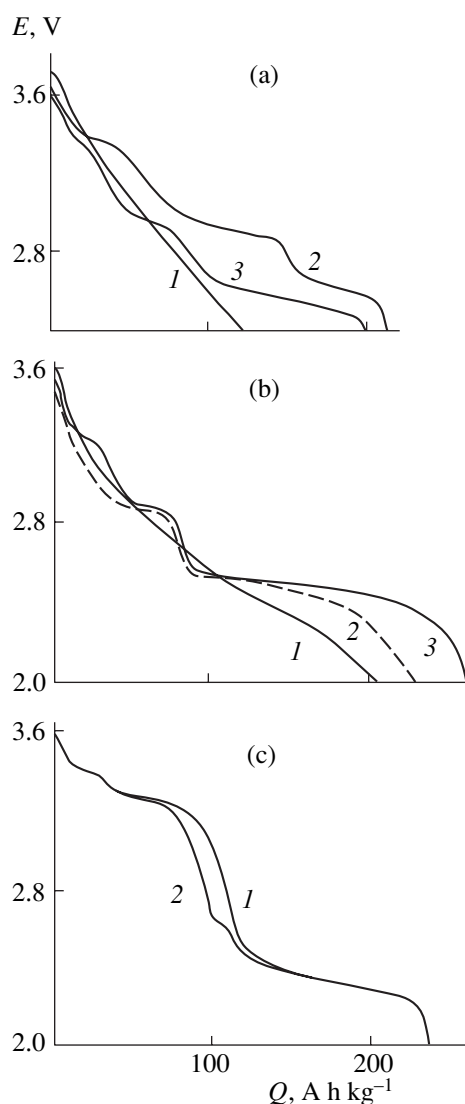


Fig. 7. Galvanostatic discharge curves for (a) ballast-free and (b, c) composite electrodes based on VOC: (1a) oxide $e\text{-V}_2\text{O}_5$ of weight $m = 2 \text{ mg cm}^{-2}$; (2a) bronze $e\text{-Na}_x\text{V}_2\text{O}_5$, $m = 1.9 \text{ mg cm}^{-2}$; (3a) $i\text{-Na}_x\text{V}_2\text{O}_5$, $m = 1.7 \text{ mg cm}^{-2}$; (1b) $e\text{-V}_2\text{O}_5$, $m = 12 \text{ mg cm}^{-2}$; (2b) $e\text{-Na}_x\text{V}_2\text{O}_5$, $m = 13 \text{ mg cm}^{-2}$; (3b) $i\text{-Na}_x\text{V}_2\text{O}_5$, $m = 14.4 \text{ mg cm}^{-2}$; (1c) $c\text{-V}_2\text{O}_5$, $m = 12 \text{ mg cm}^{-2}$; (2c) $c\text{-V}_2\text{O}_5$, $m = 19 \text{ mg cm}^{-2}$, exposed in a 0.2 M VOSO_4 solution containing 20 g l^{-1} of Na^+ ions at 20°C for 24 h and annealed at 500°C for 5 h; discharge current densities are as follows: (a) 50 and (b, c) $100 \mu\text{A cm}^{-2}$.

the course of electrolysis since the instant of formation of $e\text{-V}_2\text{O}_5$. With a currentless technique of production of $i\text{-Na}_x\text{V}_2\text{O}_5$, ionic exchange is separated in time, as compared with that occurring during the synthesis of electrolytic bronze, and starts from the instant when electrolytically produced oxide $e\text{-V}_2\text{O}_5$ is immersed into a sodium-containing electrolyte.

A quantitative synthesis of β -bronze is defined by the ion-exchange capacity of oxide $e\text{-V}_2\text{O}_5$. For non-

annealed $e\text{-V}_2\text{O}_5$, the capacity is maximum. It is considerably lower for annealed $e\text{-V}_2\text{O}_5$ (500°C) and is practically undetectable for $c\text{-V}_2\text{O}_5$. This follows from X-ray diffractometry data for the above oxides exposed in a sodium-containing electrolyte for 24 h. After the annealing of the above samples, their composition corresponds to (1) bronze (100%), in non-annealed $e\text{-V}_2\text{O}_5$; (2) a mixture of bronze (5%) and vanadium pentoxide (95%), in annealed (500°C) $e\text{-V}_2\text{O}_5$; and (3) vanadium pentoxide, in crystalline $c\text{-V}_2\text{O}_5$. The change in the color of the surface of crystallites, which is characteristic of the oxide conversion into bronze may be a conditional indicator of the capability of crystalline $c\text{-V}_2\text{O}_5$ to ionic exchange.

The difference between morphological properties and an almost 1.5-fold difference between values of specific areas (by BET) for non-annealed and annealed samples of $e\text{-V}_2\text{O}_5$ fail to convincingly explain the considerable difference existing between ion-exchange capacities of these oxides. The ion-exchange capacity of vanadium pentoxide is probably determined largely by the crystal lattice structure. X-ray diffraction patterns for non-annealed and annealed samples of $e\text{-V}_2\text{O}_5$ differ mostly in the first line of diffraction reflection, whose position correlates with the water content in the oxide. As opposed to the X-ray diffraction pattern for orthorhombic V_2O_5 (Fig. 3, pattern 1), the patterns for non-annealed $e\text{-V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ are characterized by diffuse reflection bands, which rapidly increase and slowly decrease in the direction of larger values of the reflection angle. The most intensive reflex of oxide $e\text{-V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (001) occurs in the vicinity of $2\theta = 7.8$ degrees (Fig. 3, pattern 3). The magnitude of d for this reflex is determined by the water content in the oxide. The X-ray diffraction pattern for $e\text{-V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ is similar to those for layered two-dimensional structural formations of xerogels [15] and oxide $\text{O}_3\text{-V}_2\text{O}_5$ synthesized during the oxidation of a VO_3 solution by ozone [16]. In gels, the magnitude of d diminishes with decreasing water content, specifically, d is equal to 1.155 and 0.835 nm for n of 1.6 and 0.5, respectively. The structure of gels is more open than the orthorhombic structure of $c\text{-V}_2\text{O}_5$, which allows water molecules and sodium ions to freely move in the space between layers. The probability of quantitative ion exchange increases with increasing space between layers, thus making it possible to readily carry out quantitative synthesis of β -bronze from xerogels. The magnitude of d for $e\text{-V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ diminishes with decreasing water content, just as in gels. The maximum value of d for $e\text{-V}_2\text{O}_5$ dried in air without annealing amounted in our determinations to 1.36 nm. The structural similarity between xerogels of vanadium pentoxide and electrolytic vanadium pentoxide is an important factor that explains ion-exchange properties of electrolytic vanadium pentoxide.

It makes sense to analyze results of this work on the basis of information about the cationic selectivity of dodecavanadic acid. The acid's ion-exchange proper-

ties explain many specific features of vanadium oxide compounds. The large difference between the equilibrium coefficient, specifically, $K_{\text{H}^+, \text{NH}_4^+}^{1/2} = 9.96 \pm 1.5$ and

$K_{\text{H}^+, \text{Na}^+}^{1/2} = 3.5 \pm 0.3$ [11], is broadly used in a technological procedure, where ammonium salts are introduced into solution during hydrolysis in order to prevent co-deposition of vanadium with sodium. In connection with this, the ion-exchange properties of dodecavanadic acid make it possible to explain why the authors of [17, 18] failed to electrolytically produce sodium hexavanadates from an ammonium metavanadate sodium-containing electrolyte. At the same time, owing to ion-exchange properties of dodecavanadic acid, electrolytic production of potassium metavanadate from a similar ammonium-potassium metavanadate solution seems quite viable, because $K_{\text{H}^+, \text{K}^+}^{1/2} = 11.96 \pm 0.8$. As in the presence of ammonium ions, it proved impossible to electrolytically synthesize sodium-vanadium oxide compounds from a sodium-containing electrolyte. Nor did we manage to obtain, by means of electrolysis, a lithium-vanadium oxide compound from an acid vanadyl sulfate electrolyte of pH 1.8 containing lithium ions. The lithium ions would not incorporate into electrolytic deposit of vanadium pentoxide, because average equilibrium coefficient $K_{\text{H}^+, \text{Li}^+}^{1/2}$ is small (0.4 ± 0.05). The proton links itself to the vanadium-oxygen cage of the oxide more strongly than the lithium ion.

The experimental material we presented has convincingly illustrated the predominant role of ion exchange in the production of β -bronze $\text{Na}_x\text{V}_2\text{O}_5$ on the basis of electrolytic vanadium pentoxide ($e\text{-V}_2\text{O}_5$).

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