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Manganese Dioxide Purification Methods for Producing Tantalum Capacitors with Low Equivalent Series Resistance

S. N. IVANCHENKO[1], V. Z. POIYLOV[2], A. G. STAROSTIN[2], S. V. LANOVETSKIY[2]

[1]OJSC "Elecond", Sarapul, Russia

E-mail: lsv98@mail.ru

[2]Perm National Research Polytechnic University, Perm, Russia

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Abstract

One of the main requirements for tantalum oxide semiconductor capacitors is the reduction of the equivalent series resistance (EPS), the value of which is directly related to the electrical conductivity of the semiconductor manganese dioxide layer formed on the surface of the tantalum electrode. Analysis of the current state of the production of electrolytic capacitors in Russia showed that the industry survives a steady trend towards an increase in switching frequencies from 10 to 100 kHz and higher, necessitating a reduction in the EPS of the finished capacitor. At the same time, manufactured products do not have the necessary characteristics for operation at higher frequencies. Existing technology solutions do not provide the production of high-quality capacitors since they are multistage, energy-intensive and require continuous improvement. This paper deals with the search for ways to improve the electrical characteristics of a manganese dioxide cathode coating on tantalum oxide semiconductor capacitors. A theoretical analysis of the literature was conducted in order to determine the probable causes of the increased equivalent series resistance of a capacitor. The properties of factory-made tantalum oxide semiconductor capacitors were investigated by means of X-ray phase and photomicroscopic analysis; their electrical parameters were determined. It was shown that an increase in the equivalent series resistance of capacitors is due to the presence of an impurity of high-resistance manganese oxide (III) in the composition of the cathode coating based on manganese dioxide. It was established that manganese oxide (III) contaminates the impregnating solution of manganese nitrate, from which the cathode coating on tantalum bulk-porous anodes is obtained by thermal decomposition. To reduce the EPS of the finished capacitor, a method is developed for removing manganese oxide (III) from the semiconductor coating by cleaning the precursor, manganese nitrate, and modifying the surface of the cathode coating with oxidizing agents. The proposed method can be recommended for practical implementation in the production of tantalum oxide semiconductor capacitors, which will improve the electrical characteristics by reducing the equivalent series resistance of finished products.

Keywords: oxide semiconductor capacitor, manganese dioxide, manganese oxide (III), manganese nitrate, equivalent series resistance

INTRODUCTION

Capacitors are among the mass components of modern electronic radio equipment, and the production of capacitors is an essential branch of industry. In the production of electric capacitors, a stable trend to an increase in the switching frequency from 10 to 100 kHz and higher, which causes the necessity to decrease the equivalent serial resistance (ESR) [1]. The ESR of tantalum solid electrolyte capacitors is determined by the specific bulk resistance of manganese dioxide, thickness and surface, as well as by the characteristics of transient coatings and materials used to form contact pads. The most efficient method to decrease the ESR of a capacitor is to form

cathode coating containing low-resistive manganese dioxide MnO_2 of definite phase composition.

In view of the broad range of possible valence states of manganese cation, the phase composition and structure of manganese oxides in the cathode coating is determined by the formation conditions. Similarly to many other oxides of transition metals, different crystallographic modifications of MnO_2 (α, β, γ, ε, *etc.*) with the conservation of the stoichiometric composition may have a different spatial alternation of the filled and vacant oxygen octahedrons [2], which is pronounced in the properties of MnO_2. It is known that manganese oxide of γ modification possesses the lowest specific resistance. The specific resistance (ρ) of the most widespread modification of manganese dioxide (β-MnO_2) is somewhat higher and varies within the range 70–200 Ohm · cm (Table 1) [3–6]. The gap width for γ- and β-MnO_2 is 0.58 and 0.26 eV, respectively.

The conductivity of manganese dioxide (σ) as a semiconductor is connected with the mobility of electrons (μ_n) and holes (μ_p) through the equation

$$\sigma = 1/\rho = q(N_n\mu_n + N_p\mu_p) \quad (1)$$

where ρ is specific resistance, μ_n is the mobility of electrons; μ_p is the mobility of holes; N_n, N_p are concentrations of the corresponding charge carriers; q is the elementary electric charge ($1.602 \cdot 10^{-19}$ C).

For MnO_2, as *n*-type conductor [7], electron concentration is much higher than the concentration of holes, and equation (1) looks like

$$\sigma \approx q\ \mathrm{Nn}\mu n \quad (2)$$

The electrical conduction of semiconductor MnO_2 depends on the concentrations of charge carriers and the mobility of electrons.

Another possible component of the cathode coating of tantalum solid electrolyte capacitors is manganese (III) oxide Mn_2O_3, a semiconductor with *p*-type conductivity, for which equation (1) looks like

$$\sigma \approx q\ N_p\mu_p \quad (3)$$

The specific resistance of Mn_2O_3 changes substantially from one sample to another, which is characteristic of manganese oxides; it is within the range 10^4–10^6 Ohm · cm as average, with rather small energy of conductivity activation (~0.1 eV) [8].

TABLE 1

Specific resistance of manganese dioxide of different modifications [7]

Modification of MnO_2	ρ, Ohm · cm
γ-MnO_2	20–50
β-MnO_2	70–200
δ-MnO_2	>500 000

So, the available information on the conductivity of manganese oxides allows us to conclude that the optimal component of cathode coating is γ-MnO_2, while an increase in Mn_2O_3 content in the cathode coating of a capacitor may lead to an increase in its resistance.

The formation of Mn_2O_3 impurity occurs during the thermolysis of the precursor, which is manganese nitrate. Results of the studies into the decomposition of manganese nitrate and the methods used to govern this process for the purpose of forming an oxide coating with the required characteristics are reported in [9–11]. At the initial stage of heating the solution of the precursor, the removal of unbound and crystal water is accompanied by salt hydrolysis, resulting in the formation of manganese hydroxonitrate. During further heating of the solution, $Mn(OH)NO_3$ is oxidized to manganese metahydroxide MnO(OH), which is transformed into MnO_2 at a temperature of 250–270 °C, or into Mn_2O_3 in the case of the lack of oxygen. So, Mn^{2+} ions are stage by stage oxidized in the redox reaction at first into Mn^{3+}, and then into Mn^{4+}. Understanding of the mechanism of thermolysis of $Mn(NO_3)_2$ solutions allowed determination of the optimal conditions for the formation of low-resistive MnO_2 [12–14]. However, a connection between the phase composition of the semiconductor coating and the ESR characteristics of the capacitor was not established in the works cited above and in other publications.

The goal of the present work was to evaluate the effect of the phase composition of the cathode coating obtained from the technological solutions on manganese nitrate on the ESR of the solid electrolyte tantalum capacitors and to search the ways to obtain high-quality cathode coating on the basis of manganese oxide with low ESR.

EXPERIMENTAL

Worked out and regenerated solutions of manganese nitrate from the return cycle of the impregnation of porous tantalum electrodes were used in the studies. Regeneration of manganese solutions was carried out using the solutions of nitric acid and hydrogen peroxide.

The cathode coating was formed through the impregnation of porous tantalum electrodes 4.4 × 3 × 1 mm in size for 3 min in the solutions of

manganese nitrate with the required concentration (25–71 mass %) and subsequent pyrolytic decomposition of the solution in a muffle furnace at a temperature of 250 °C for 3 min.

After the deposition of standard contact layers, the measurement of the electric parameters of resulting products was carried out according to GOST 28885–90. The determination of ESR was performed with the help of an LCR 4263B meter (Agilent Technologies) at the frequency of 100 kHz.

The phase composition of crystalline precipitates obtained from the worked out manganese impregnation solutions and the cathode coating was evaluated with the help of a Shimadzu XRD-7000 X-ray diffractometer. X-ray diffraction patterns were processed using the software XRD 6000/7000 ver. 5.21 and the software product SIROQUANT ver. 4. Photo microscopic analysis of the cathode coating was carried out using a Carl Zeiss Axio Imager M2.m optical microscope with the magnification up to 4000, equipped with a digital camera Carl Zeiss AxioCam MRc5.

RESULTS AND DISCUSSION

Within the studies of the formation conditions for the components of semiconductor coating, we carried out the X-ray phase analysis (XPA) of the crystalline precipitate obtained as a result of crystallization of the impregnating solution of manganese nitrate after operation for 6 months at the technological line of the production of solid electrolyte tantalum capacitors (Fig. 1).

The XPA of the crystalline precipitate revealed the presence of a large amount of the admixtures of manganese oxides and nitrides: MnN, Mn_4N, MnO_2, MnOOH, Mn_2O_3, MnO. All these impurity compounds except MnO_2 are characterized by low electric conductance [15].

It was established on the basis of XPA data that among the compounds identified in the crystalline product, those remaining after the thermolysis of $Mn(NO_3)_2$ in the cathode coating are Mn_2O_3 and ε-MnO_2, composed of disordered crystals of γ-MnO_2 [16].

The fine particles of manganese (III) oxide getting through impregnation onto the surface of tantalum cathodes act as the centres of Mn_2O_3 crystallization during thermolysis. In turn, this leads to an increase in the content of the manganese (III) oxide phase in the cathode coating and, as a consequence, to the high ESR of the capacitor. Therefore, it is possible to reduce the ESR of the capacitor by removing Mn_2O_3 or decreasing its content in the precursor and/or in the coating.

The first possible method to decrease the content of manganese (III) oxide in the solid electrolyte is its removal from the precursor by the treatment with a mixture of oxidizers (HNO_3 and H_2O_2) [17]:

$$Mn_2O_3 + 4HNO_3 + H_2O_2 = 2Mn(NO_3)_2 + 3H_2O + O_2 \quad (1)$$

A mixture of the aqueous solutions of hydrogen peroxide and nitric acid, both possessing a high oxidative potential and containing no atoms of other elements except those already present in the contaminated solution was chosen as the oxidizer.

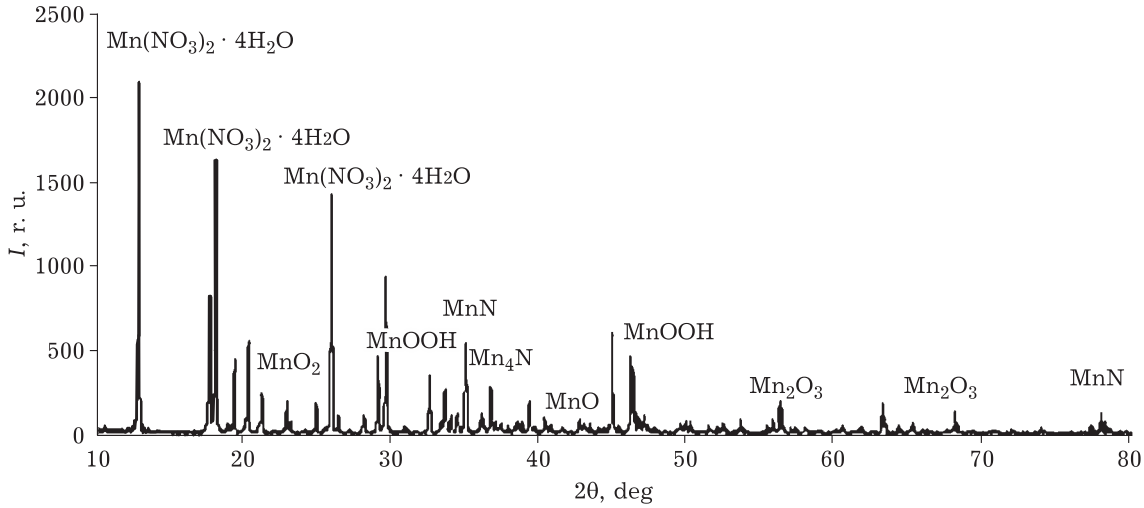

Fig. 1. X-ray diffraction patterns of the crystalline precipitate obtained from the solution of $Mn(NO_3)_2$.

Reaction (1) proceeds with the high completeness and thermodynamic probability within a broad temperature range. Within the calculation temperature range 273–573 K, the change of Gibbs energy for reaction (1) has a negative value (from −117.2 to −83.6 kJ, respectively), and the equilibrium constant is significant.

According to the conditions of reaction (1), regeneration of the 71 % worked out solution of manganese nitrate was carried out by the addition of the 0.5 % solution of H_2O_2 and HNO_3 in portions with periodic measurements of solution pH until the value within the range 2.6–2.8 was achieved. After this procedure, pH of the treated solution, the content of the major substance and the concentration of insoluble particles corresponded to the parameters of fresh $Mn(NO_3)_2$ solutions.

To estimate the effect of the regeneration of impregnating solution on the ESR of tantalum capacitors, a series of experiments on obtaining the solid electrolyte tantalum capacitors was carried out, with the use of worked out impregnating solutions circulating in the technology (version 1) and regenerated (version 2) solute ions of manganese nitrate. The ESR values of the resulting capacitors with the nominal voltage 10 V and capacity 100 μf are presented in Table 2. One can see that ESR value for capacitors manufactured from the regenerated solution of manganese nitrate is higher by 37 %. This positive effect is first of all connected with a decrease in the fraction of high-resistance Mn_2O_3 in the precursor.

Another promising direction to decreased ESR of capacitors is the direct removal of Mn_2O_3 from the cathode coating. According to the data reported in [18], Mn_2O_3 is a derivative of manganese (II) and manganese (IV). For this reason, manganese (III) oxide exhibits the properties of both a base and an acid; it disproportionates in the presence of diluted nitric acid with the formation of manganese dioxide and manganese nitrate [19] according to the reaction

$$Mn_2O_3 + 2HNO_3 = MnO_2 + Mn(NO_3)_2 + H_2O \quad (2)$$

This reaction proceeds spontaneously in the forward direction within a broad temperature range. The rate of manganese (III) oxide disproportionation is described by the theory of topochemical reactions and is connected with the interphase area [19, 20]. In addition, the completeness of reaction (2) depends on temperature and component concentrations. The effect of the concentration of nitric acid on the completeness of reaction (2) and on the change in the ESR of tantalum capacitors was studied in the experiments that have been carried out within the present work. For this purpose, the sections of tantalum solid electrolyte capacitors with semiconductor coating based on manganese dioxide were manufactured, with the nominal voltage 2.5 V and nominal capacity 500 μf. Then the formed cathode coatings were treated in the solutions with different concentrations of nitric acid, from 15 to 45 mass %, at a temperature of 22 °C for 1 min, and then the sample was dried for 20 min at a temperature of 150 °C. After the treatment of the semiconductor coating, contact layers were deposited to provide the possibility of measuring the electric characteristics of the sections. The results of ESR measurements for capacitor sections are listed in Table 3. One can see that the most substantial decrease in the ESR of tantalum solid electrolyte capacitors is observed after the treatment of the semiconductor coating with a 45 mass % solution of HNO_3. The XPA data revealed that Mn_2O_3 present in the initial coating is transformed into pyrolusite (β-MnO_2) after the treatment with a 45 % solution of nitric acid.

The treatment of the cathode coating of tantalum solid electrolyte capacitors may be also carried out with a mixture of hydrogen peroxide and nitric acid according to reactions

$$MnO_2 + 2HNO_3 + H_2O_2 = Mn(NO_3)_2 + 2H_2O + O_2 \quad (3)$$

$$2Mn_2O_3 + 8HNO_3 + 2H_2O_2 = 4Mn(NO_3)_2 + 6H_2O + 2O_2 \quad (4)$$

The concentrations of reagents (HNO_3, H_2O_2) should provide the possibility to remove the

TABLE 2

ESR of capacitors obtained from circulating and purified $Mn(NO_3)_2$ solutions

Version	Precursor for the formation of cathode coating	ESR, mOhm
1	Circulating $Mn(NO_3)_2$ solution	490±12
2	Regenerated $Mn(NO_3)_2$ solution	311±7

TABLE 3

ESR of the sections of capacitors obtained under different conditions of the treatment of semiconductor coating

Version	Formation of cathode coating	ESR, mOhm
1	Without the treatment of coating	99.0±11.3
2	Treatment of coating with HNO_3, 15 mass %	77.0±8.8
3	The same, 30 mass %	77.0±8.8
4	The same, 45 mass %	62.0±9.6

defective regions of the manganese oxide coating without a substantial decrease in the effective thickness of the cathode layer. In the course of reactions (3), (4), the fragments of the coating possessing the excess surface energy are prone to dissolution. These include defect-bearing sites: cleaved facets, cracks, bulgings. The conditions of the cathode coating treatment with a mixture of nitric acid and hydrogen peroxide are identical to those involved in the experiments with the treatment in nitric acid.

The results of the studies confirmed the efficiency of surface modification of the cathode coating with the indicated mixture of oxidizers. The equivalent serial resistance of capacitor sections with the nominal resistance 20 V and capacity 22 μF decreased by 29 % after the treatment, and the defect content of the coating decreased. The photomicroscopic analysis of the modified coating (Fig. 2, *a*) showed that its surface is more uniform than the initial coating (see Fig. 2, *b*).

X-ray diffraction patterns (Fig. 3) provide evidence of a 2–3 fold decrease in the intensity of the peaks of manganese (III) oxide in the cathode coating after the treatment according to the proposed procedure. Analysis of the data obtained by means of X-ray analysis with the help of the SIROQUANT ver. 4 software product showed that the content of the Mn_2O_3 phase in the cathode coating treated with the solution of nitric acid and hydrogen peroxide decreased by 23 % in comparison with the cathode coating obtained without treatment.

CONCLUSION

It was established that an increase in ESR of tantalum solid electrolyte capacitors is connected

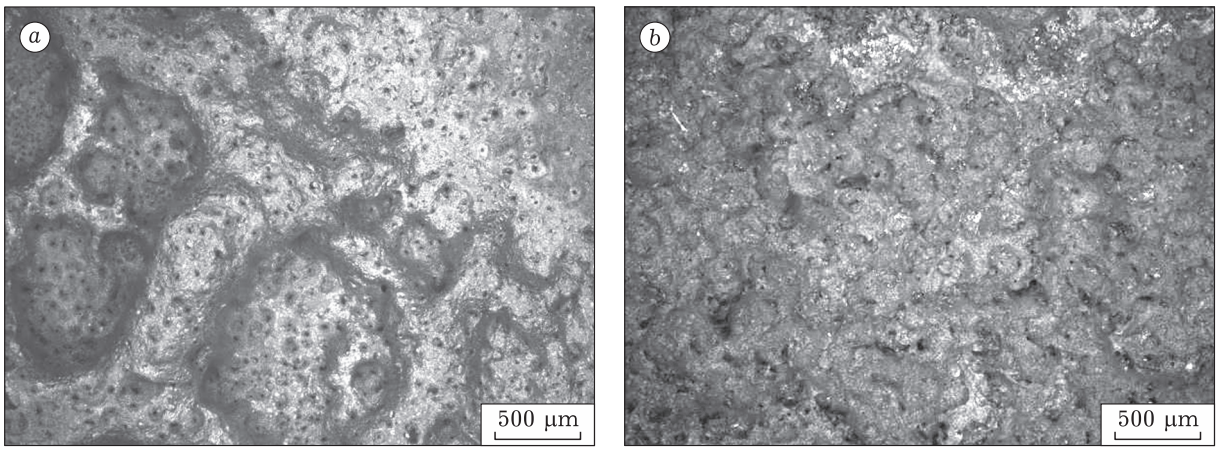

Fig. 2. Results of the photomicroscopic analysis of the surface of coating sample before (*a*) and after (*b*) treatment with reagents.

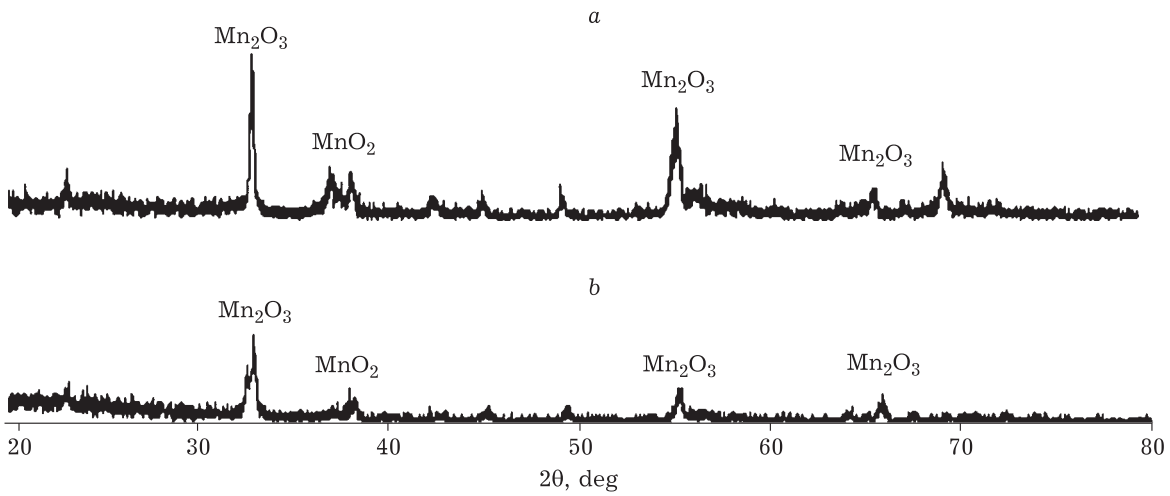

Fig. 3. X-ray diffraction patterns of the cathode coating: *a* – treated in the solution of HNO_3 and H_2O_2, *b* – without treatment.

mainly with the presence of fine Mn_2O_3 particles in the circulating solution of the precursor, $Mn(NO_3)_2$, from which the cathode coating is formed. It is possible to decrease the ESR of the capacitor by removing Mn_2O_3 or by reducing its content in the solution of the precursor, and/or in the semiconductor coating. Thus, the ESR of capacitors manufactured from the purified solution of manganese nitrate is lower by 37 %.

The treatment of the coating, composed of manganese dioxide with the admixture of Mn_2O_3, deposited on tantalum anodes, allows a decrease in the resistance of the capacitor both due to the change of the phase composition during the treatment with nitric acid and due to the modification of the surface of cathode coating through partial dissolution of the cathode coating with defects in the solution of a mixture of nitric acid and hydrogen peroxide.

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