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Capacitive properties of composite electrodes based on polyaniline and nanoporous titanium oxide obtained by plasma-electrolytic oxidation

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Abstract. The capacitive characteristics of composite electrodes based on nanoporous titanium oxide obtained by plasma electrolytic oxidation are considered. It is shown that the specific capacitance of a multilayer supercapacitor based on formed titanium oxide and polyaniline (PANI) is 10 mF/cm^2. The resulting oxide layers have a crystalline structure, providing minimal faradaic resistance, which is promising for use in electrochemical double-layer supercapacitors.

Keywords: titanium, electrolyte plasma, nanoporous oxide, polyaniline, supercapacitor

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Емкостные свойства композитных электродов на основе полианилина и нанопористого оксида титана, полученного методом плазменно-электролитического оксидирования

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Аннотация. Рассмотрены емкостные характеристики композитных электродов на основе нанопористого оксида титана, полученного методом плазменно-электролитического оксидирования. Показано, что удельная емкость многослойного суперконденсатора на основе сформированного оксида титана и полианилина (ПАНИ) составляет 10 мФ/см^2. Полученные оксидные слои имеют кристаллическую структуру, обеспечивая минимальное фарадеевское сопротивление, что является перспективным для использования в электрохимических двухслойных суперконденсаторах.

Ключевые слова: титан, электролитная плазма, нанопористый оксид, полианилин, суперконденсатор

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Introduction

Research and development of high-capacity components and systems are important and rapidly developing areas in modern electronics. To increase the effective area of electrodes of electrochemical capacitors, materials with a highly developed surface are used. Such electrodes are usually formed on the basis of activated carbons [1], carbon nanotubes [2], nanoporous metal oxides [3] and other materials. These materials can significantly increase the specific capacity of devices, improve their energy characteristics and provide a higher charging rate. An important aspect is also ensuring the stability and durability of electrode materials during multiple operating cycles. Modern research is aimed at developing new composite materials, methods for their synthesis and processing, as well as optimizing the structure to achieve maximum efficiency and reliability of high-capacity electrochemical systems. In this paper, the characteristics of supercapacitors based on nanoporous titanium oxide obtained by plasma electrolytic oxidation (PEO) will be considered.

Materials and Methods

Titanium with a purity of 99.7% was used to study the features of plasma electrolytic oxidation (PEO). Porous titanium oxide was obtained by plasma electrolytic treatment in a 1 M aqueous solution of sulfuric acid, the technique is described in [4]. Then, each electrode was chemically coated with a layer of emeraldine form of polyaniline, and a solution of polyvinyl alcohol with 3.4 M orthophosphoric acid served as a layer between the electrodes. The capacitive characteristics of the obtained structures were determined by cyclic voltammetry (potentiostat-galvanostat P-45X) in the range from –0.5 to 0.5 V at potential scan rates from 20 to 100 mV/s. Impedance spectra were recorded in the frequency range from 0.1 Hz to 50 kHz with an amplitude of 50 mV. The EIS Spectrum Analyzer software based on the Levenberg-Marquardt algorithm with amplitude minimization was used for their analysis. The surface morphology of the oxide layers was analyzed using scanning electron microscope (PHENOM PRO-X). A Bruker D2 Phaser diffractometer was used for qualitative and quantitative phase analysis of the samples.

Results and Discussion

The electrolyte used to obtain titanium oxide nanotubes largely determines the characteristics of the structures formed on the metal surface. In this work, an analysis of the structures obtained using an aqueous solution based on sulfuric acid was carried out. A distinctive feature of PEO from conventional oxidation of metals is that when a certain voltage is reached, a breakdown of the screening gas bubbles occurs with the formation of plasma.

The formation of pores (average size ~ 110 nm) in titanium oxide (Fig. 1, *a*) is due to the implementation of extreme conditions during the processing, namely, an increase in the chemical activity of the solution near the anode [4].

The discharges observed visually on the electrode surface move along the surface. Such discharges exist for a rather short time, but this time is sufficient for the polymorphic transformation of the oxide layer from an amorphous state to a crystalline one. This is confirmed by the data of X-ray structural analysis (Fig. 1, *b*).

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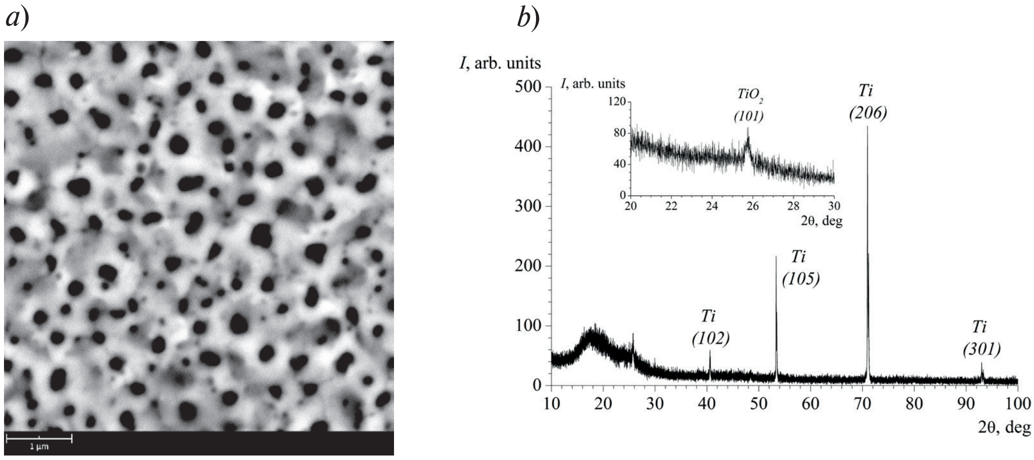

Fig. 1. Characteristics of nanoporous titanium oxide obtained by the PEO method: SEM image of the surface (*a*); diffraction pattern (*b*)

The capacitive properties of the supercapacitor formed on the basis of the obtained electrodes with porous titanium oxide were estimated by cyclic voltammograms, a typical form of which is shown in Fig. 2, *a*. The specific capacitance of the obtained electrodes was ~ 10 mF/cm² (at a scanning rate of 20 mV/s). The specific capacitance value of such structures, depending on the degree of modification, can reach ~ 6–7 mF/cm² [5].

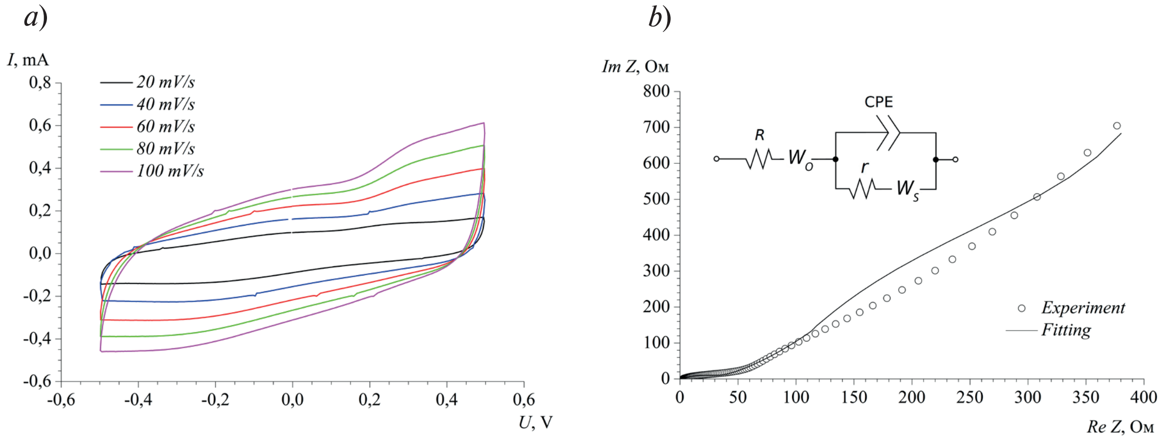

Fig. 2. Capacitive characteristics of the obtained electrodes: cyclic voltammograms (*a*) and electrochemical impedance spectra. The inset shows the equivalent circuit (*b*)

The structural features of the functional layers of the formed multilayer capacitive systems were judged by the impedance spectroscopy data. The Im Z (Re Z) dependencies (Fig. 2, *b*) are typical for capacitors and have sections with a shape close to a semicircle, which characterizes the Faraday resistance value, which is 32 Ohm, which is 6 times less than the electrodes obtained in 0.6 wt. % HF [6]. The end point of the high-frequency region of the obtained impedance spectra is determined by the active resistance R of the systems under consideration, which lies in the range of 1.5 ... 2 Ohm. The nanostructured nature of the electrodes used determines the shape of the impedance in the low-frequency region and is described by a constant-phase element – CPE $(Z_{\text{CPE}} = C_\alpha^{-1}(j\omega)^{-\alpha})$. In addition to the surface roughness, diffusion processes occurring in the interelectrode space have a significant effect on the nature of the recorded spectra. To describe these processes, Warburg elements were introduced into the equivalent circuit. Element W_S is characterized by the impedance of finite diffusion with a transmitting boundary, element W_O – is characterized by a reflecting boundary, and $b_{S,O} = \frac{d}{\sqrt{D}}$ (d – is the thickness of the Nernst diffusion layer, D – is the ion diffusion coefficient):

$$Z_{W_S} = \frac{W_S}{\sqrt{\omega}}(1-j)\tanh\left(b_S\sqrt{j\omega}\right), \tag{1}$$

$$Z_{W_O} = \frac{W_O}{\sqrt{\omega}}(1-j)\coth\left(b_O\sqrt{j\omega}\right). \tag{2}$$

Table

Equivalent circuit parameters

Parameter	R, Ohm	r, Ohm	C_α 10^{-5} $s^\alpha \cdot Ohm^{-1}$	α	W_S, $Ohm \cdot s^{-1/2}$	b_s, $s^{-1/2}$	W_O, $Ohm \cdot s^{-1/2}$	b_O, $s^{-1/2}$
Value	1.98	32	6.13	0.65	210	1.43	0.16	0.007

Analysis of the parameters obtained during approximation showed high diffusion permeability (Table) of supercapacitors based on electrodes with nanoporous titanium oxide obtained by the PEO method.

Conclusion

Thus, in this work, nanostructured electrodes based on porous titanium oxide were created by the method of plasma-electrolytic oxidation of titanium. It is shown that the obtained composite electrodes in the supercapacitor structure have a specific capacity of 10 mF/cm^2. The obtained electrodes have a low faradaic resistance (32 Ohm), which is promising for use in electrochemical double-layer supercapacitors.

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