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SYNTHESIS OF NONSTOCHIOMETRIC NANO-NbC
AND ITS ELECTROCHEMICAL PERFORMANCE

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An important reason making NbC_y an object of research was a significant practical value of nanostructured nonstoichiometric carbides as temperature-stable construction and functional electrocatalytic materials. This compound is an object of interest as a model material from the fundamental point of view due to NbC_y contains structural vacancies in its nonmetallic sublattice, thus the concentration of vacancies effects on structure and properties of the substance. In earlier works [1, 2] nanostructured nonstoichiometric niobium carbides with a crystallite size of about 23 nm were studied, they were obtained by the electrochemical method, but chemical synthesis methods are not mentioned in the literature. Development of a method for producing nanosized particles is a theoretically and practically important task, therefore, the aim of this work was to develop a technique aimed at producing nanostructured niobium carbide with a crystallite size below 10 nm and studying its electrocatalytic performance during the ethanol reforming process.

The phase composition of synthesized powders was verified via X-ray diffractometry, surface morphology was measured with scanning electron microscopy. The specific surface and porosity of niobium carbide were measured using BET analysis; the density of the powders was determined using a helium pycnometery. The electrocatalytic properties of the sample were studied by cyclic voltammetry during the electrolytic reforming of ethanol, accompanied by the evolution of hydrogen. To estimate the catalytic activity from the linear part of the obtained profiles, the Tafel slopes were calculated, and impedance spectra in Nyquist coordinates were obtained to reveal the reaction mechanism of the electrochemical process.

Dark-grey powders were obtained by thermal treatment of niobium citrate at 1200°C in a vacuum. According to XRD data, annealed niobium carbide powders have type B1 cubic structure (JCPDS card 000-38-7167) with an average crystallite size of 9 nm. A detailed synthesis scheme is shown in Figure 1.
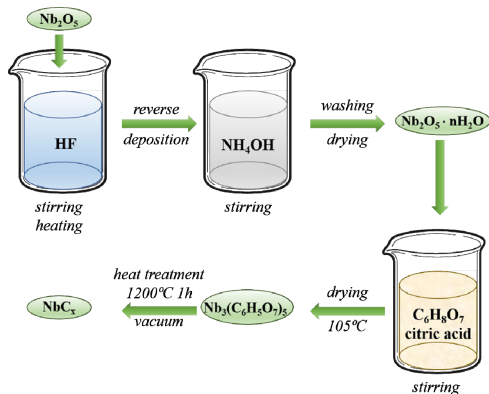
Figure 1. The synthesis scheme of nanostructured non-stoichiometric niobium carbide NbC_y.

It was found that the specific surface area of the samples is 211.9 m^2/g, and the average pore volume is 0.019 cm³/g. It is shown that the obtained niobium carbide is an effective catalyst for electrocatalytic reforming of ethanol. Based on voltammetry, it was found that the overvoltage after 1 cycle is only 250 mV (at 10 mA/cm^2), and the overvoltage after 500 charge-discharge cycles increased by only 21 mV from the initial one. The Tafel slope for the NbC_y sample after 1 and 500 charge-discharge cycles was 135 and 90 mV/dec, respectively. The results of cyclic voltammetry indicate high stability of the obtained sample, which is also confirmed by chronoamperometry, it results in the decrease of the current density during the hydrogen evolution reaction by only 5% of the initial value over 20 hours (Figure 2).
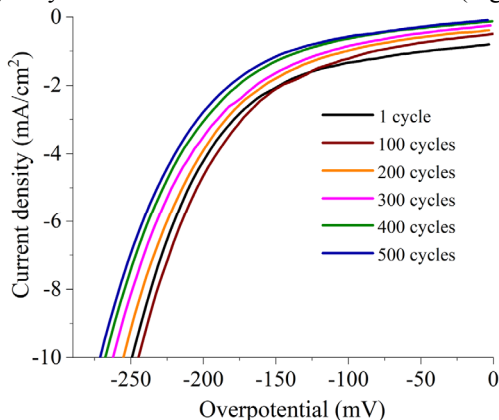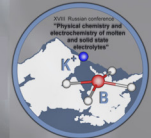

Figure 2. NbC_y cyclic stability polarization curves obtained by a linear potential sweep at a rate of 10 mV/s.

Thus, as a result of this work, the possibility of synthesis of nanostructured non-stoichiometric niobium carbide as a result of a simple and effective method for the thermal treatment of niobium citrate in a vacuum medium and the prospects of its further use as the basis for electrocatalytic materials was shown.

References

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ON THE USING OF CITRATE COMPLEX TOWARD THE SYNTHESIS OF α-Ni/β-Co NANOELECTROCATALYSTS

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Efficient hydrogen production by electrolysis of aqueous and aqueous alcohol solutions is based on the use of electrode materials with a low overpotential of hydrogen evolution reaction (HER) [1,2]. When rejecting expensive materials containing noble metals (Pt, Pd, etc.), coatings consist of metals of the iron triad obtained by electroplating method on the activated surface of the substrate (nickel foam, carbon fibers) are used [3-5]. Among the numerous methods of obtaining a coating (layer by layer (SILD, SILAR), vacuum spraying, electrophoresis, etc.), electrodeposition is the simplest and most controllable method. However, there is a problem with the size of the crystallites and the coating degree of the substrate, which affects the electrocatalytic characteristics. The use of simple (non-complex) electrolytes doesn't solve these tasks

This study is devoted to the preparation of composite coatings α-Ni/β-Co from a complex citrate electrolyte by electrodeposition on carbon felt and testing of them in an aqueous alcohol solution of 1M KOH. The electrolyte compositions are shown in Table 1. The pH effect of the electrolyte on the