Structural and Electrocatalytic Properties of Pt/C and Pt–Ni/C Catalysts Prepared by Electrochemical Dispersion

N. V. Smirnova, A. B. Kuriganova, D. V. Leont’eva, I. N. Leont’ev, and A. S. Mikheikin

Abstract—The structural and electrocatalytic properties of Pt/C and Pt–Ni/C catalysts prepared by the electrochemical dispersion of metals under the action of pulse alternating current in a solution of NaOH were studied. Using X-ray diffraction analysis and scanning and transmission electron microscopy, it was found that the synthesized Pt/C catalysts contained active constituent particles with the average size $D_{111} = 10.6$ nm with a predominantly cubic shape. Upon the dispersion of a Pt$_3$Ni alloy, the Pt–Ni/C catalyst containing the particles of a stoichiometric metal phase of Pt$_3$Ni ($D_{111} = 9.6$ nm) and also Pt$_3$Ni particles ($x > 3$) enriched in platinum ($D_{111} = 8.1$ nm). The synthesized catalysts possessed high electrocatalytic activity and stability in the reaction of methanol oxidation. The characteristics of these catalysts as anodes in the membrane-electronic unit of a hydrogen–air solid-polymer fuel cell were studied.

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INTRODUCTION

Alternative methods, including electrochemical ones, are of importance for solving the energy and environmental problems facing the human society. The development of electrochemical power engineering in many respects depends on advances in the elaboration of active and stable nanomaterials for the cathodes and anodes of fuel cells. Low-temperature solid-polymer fuel cells (SPFCs), in which the oxidation of hydrogen or simple organic molecules (for example, methanol) occurs on the anode and the reduction of oxygen, on the cathode, are considered highly effective and ecologically sound energy sources [1]. Platinum-containing metal–carbon composites are the best materials for preparing anodic and cathodic catalysts as the constituents of SPFCs [2, 3].

As a rule, the reduction of oxygen on the cathode occurs more slowly than the majority of anodic reactions. Furthermore, products capable of activating the processes of catalyst, proton-conducting polymer electrolyte, and membrane degradation are formed on the cathode. Among these products are various chemisorbed oxygen species $O_{ads}$ and $OH_{ads}$, which are formed as a result of water electrochemisorption, and hydrogen peroxide—the product of the two-electron reduction of oxygen. Therefore, the service life and performance characteristics of fuel cells depend to a considerable degree on the electrochemical properties of the cathode. The preparation and use of the alloys and intermetallic compounds of platinum with nickel [4–6] and other transition metals [7, 8] is a promising method for solving the above problems. The specific catalytic activity of such binary systems increases due to a change in the surface geometry (a decrease in the Pt–Pt interatomic distance in crystal lattice, which facilitates the adsorption of $O_2$ [9] and the development of the metal surface as a result of leaching the second component [7]) and electronic properties (a change in the oxidation state of platinum [10] and the formation of a new electron structure with a high concentration of vacancies in 5$d$ orbitals [9]).

The anode in fuel cells presents a less burning problem, which mainly consists in the necessity of increasing the rate of oxidation of simple organic compounds (for example, methanol) and, most importantly, increasing the resistance of a catalyst to poisoning by the products of the chemisorption of organic compounds, primarily CO. This is also true for SPFCs because hydrogen obtained by the conversion of methane always contains CO, although its amounts are insignificant. This problem can be solved by the following two methods: the use of Pt–M binary systems, where M is the metal that adsorbs oxygen (Ru, Sn, etc.) [11, 12] or the application of a Pt/C catalyst whose active constituent (Pt) particles have a specific shape and hence crystallographic orientation, which to a certain degree prevents their CO poisoning [13].

Many physical and chemical (reduction) methods, including electrochemical ones, for the synthesis of nanosized metal particles and catalysts on their basis are well known [14]. The traditional method of the electrodeposition of metals onto carbon supports makes it possible to obtain highly dispersed particles (15–30 nm), but it is applicable only to stationary sup-
ports [15] and unsuitable for the synthesis of powdered metal—carbon materials. On the electrochemical deposition of a metal, its ions are discharged on the cathode surface. With the use of a suspension of powdered carbon support as an electrolyte even in a high concentration and with intense stirring, it is impossible to make reliable contact of support particles with the cathode. It is likely that a portion of support particles can come into contact with the cathode surface, and the platinum ion can be discharged on the support surface rather than on the electrode in certain circumstances. However, the amount of these particles is negligibly small in comparison with the amount of metal deposited on the surface of the cathode. Tian et al. [16] proposed a method based on electrochemical processes for the preparation of intricately shaped platinum particles. On applying rectangular current pulses of alternating polarity, spherical platinum particles to 700—900 nm in diameter undergo selective dissolution with the formation of 24-hedrons with high-index faces like {210}, {310}, and {520}.

The phenomenon of the destruction of metals in alkaline solutions on cathodic polarization has been known for more than 100 years [17]. The destruction of platinum under the action of harmonic alternating current was discovered in the 1970s; the effects of the nature and concentration of an electrolyte, temperature, and harmonic alternating current frequency and density were determined [18]. Because of the development of nanotechnologies, interest in this process has quickened in the past few years. Methods for the preparation of platinum sols [19, 20] and platinum—carbon catalysts [21, 22] by the electrochemical dispersion of platinum foil under the action of alternating current were proposed. The possible mechanisms of this process were discussed in publications [23, 24]. The processes of the cathodic insertion of an alkali metal into platinum with the formation of an intermetallic compound and its subsequent degradation as a result of interaction with water play an important role in these mechanisms [25]. With the use of a current of variable polarity, various chemisorbed oxygen species and even phase platinum oxide can be formed on the anode. The release of hydrogen on the cathode facilitates the dispersion of the metal and the reduction of the oxide. The detailed analysis of the mechanism of platinum dispersion under the action of alternating current is beyond the scope of this study, and it will be discussed separately. Here, we consider the structural and electrocatalytic properties of Pt/C and Pt—Ni/C prepared by an electrochemical dispersion method.

EXPERIMENTAL

Electrochemical Synthesis of Pt/C and Pt—Ni/C Catalysts

The synthesis of metal—carbon catalysts was carried out in accordance with a published procedure [22, 24]. Electrodes made of foil (of platinum or a Pt3Ni metallurgical alloy for preparing Pt/C or Pt—Ni/C, respectively) with the same surface area of 5 cm² were placed in a suspension with 3 wt % Vulcan XC—72 carbon support (Cabot Corp., the United States; $S_{np} = 240 m^2/g$) in a 2 M aqueous solution of NaOH. In an undivided cell with continuous stirring, symmetrical pulse alternating current with a frequency of 50 Hz (pulse duration, 2.5 ms) was impressed to the electrodes; the average current density was 0.2 A/cm. The temperature was maintained at a constant level of 30—35°C. The concentrations of active constituents (Pt and Pt3Ni) in the catalyst were determined based on the duration of the synthesis, knowing the preliminarily measured rate of the dispersion of electrodes. After the synthesis, the suspension was filtered, and the catalyst was washed with distilled water to a neutral pH value of wash water and dried at 80°C for 1 h.

Characterization of the Composition and Structure of the Catalysts

The X-ray diffraction patterns of the synthesized catalysts were obtained in the Swiss—Norwegian Beam Lines at the European Synchrotron Radiation Facility (SNBL ESRF). A procedure analogous to that described by Leontyev et al. [26] was used to obtain the X-ray diffraction patterns and to calculate unit cell parameters and average nanoparticle sizes.

The microscopic studies of the catalysts were conducted on a Zeiss Supra 25 field emission scanning electron microscope (Carl Zeiss AG, Germany) and a Zeiss LEO 912AB (Carl Zeiss AG) transmission electron microscope.

For determining the concentrations of active constituents in the synthesized catalysts, we used an integrated approach—we studied not only the prepared catalysts but also the electrodes subjected to dispersion and electrolyte solutions after the synthesis. The following methods were used for this purpose:

— the thermogravimetric analysis of catalysts on an STA 409 Luxx simultaneous thermal analyzer (Netzsch, Germany) at a heating rate of 5 K/min from room temperature to 1000°C in air;

— energy dispersive X-ray microanalysis (EDAX) on a Quanta 200 SEI instrument (FEI, the Netherlands);

— the measurement of the weight losses of Pt and Pt3Ni electrodes after the synthesis;

— the spectrophotometric analysis of the electrolyte after the synthesis of a catalyst for determining the concentrations of platinum and nickel ions formed as a result of the dissolution of electrodes with the aid of a SPECOD UV—VIS spectrophotometer (Carl Zeiss).

Each of the above individual methods is insufficiently reliable for determining the composition of a