Active technological control of synthesis of high-active catalysts on the surface of solid electrolytes of fuel elements

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Abstract. The method of active process control of parameters of synthesized catalysts on electrolytes of solid oxide fuel cells is considered. Using the proposed method, it is possible to obtain a catalyst with a maximum active area. This leads to an increase in the power of the fuel cell. Also, due to carrying out the technological process in strict compliance with the specified optimal parameters, good adhesion of the catalyst to the surface of the solid electrolyte is achieved. It leads to extending of service life of the solid oxide fuel cells. Experimental studies using the proposed method and its measuring control system showed the possibility of obtaining catalysts with minimum deviations from the specified optimal parameters.

1. Introduction

Production The production of the fuel cells is a multi-staged technological process. Therefore to obtain fuel cells with specified parameters, it is necessary to carry out technological control at all main stages. In most cases, only the operational parameters of the fuel cells after their final assembly are determined. It results in reducing the yield of suitable fuel cells and in a relatively large variation of parameters in different batches. In this paper we will consider the solid oxide fuel cells, in which the electrolyte is an ion-conducting oxide ceramic (solid electrolyte) [1]. This type of fuel cell is used in medium and large power stations because it is able to work on various types of hydrocarbon fuels and does not require the use of expensive platinum as a catalyst [2]. One of the main limitations for the wide use of fuel cells of this type in low power and portable equipment is their high operating temperature of 500-900°C [3]. This requires good heat insulation of the fuel cells, resulting in an increase in weight and size parameters as well as a relatively short service life compared to fuel cells on polymer proton-conducting membranes [4]. Fuel cells based on polymer proton-conducting membranes require the use of platinum or palladium for their effective operation [5]. Recently, there are works aimed at reducing the cost of fuel cells on polymer proton-conducting membranes, but still for their long-term operation, pure hydrogen is required as a fuel [6]. Solid oxide fuel cells have the main advantage that they can operate on various hydrocarbon fuels and at the same time are less demanding on purity fuels [7]. The operational parameters of the finished solid oxide fuel cell is also affected by factors such as the uneven thickness of the solid oxide electrolyte, the uneven application
of the catalyst to the surface of the solid oxide electrolyte, and the insufficient adhesion of the catalyst to the surface thereof [8].

In order to create fuel cells with a large technological resource and specific power, it is necessary to carry out technological control at the main stages of their production. Traditionally, the solid electrolyte is obtained by sintering the powder [9]. In order to provide efficient operation of the solid oxide fuel cell, two basic electrolyte requirements must be met: it must be thin to reduce ohmic losses and at the same time gas-tight to prevent direct mixing of fuel and oxidant. To date, the production of fuel cells has practically reached the technological limit on the thickness of the solid electrolyte, which makes it impossible to increase the specific power in this direction.

Also, the specific power is directly affected by the rate of oxidation and reduction reaction on the electrodes of the fuel cell, which is determined by the temperature in the reaction zone and catalytic activity of the catalyst [10]. The maximum operating temperature of the fuel cells is determined by the heat resistance of the structural materials used in them. The minimum operating temperature is determined by the need to provide the required reaction rate and therefore the acceptable specific power [11]. In this context, a pressing task is to increase the specific power of the solid oxide fuel cells and, as a result, to reduce the weight and size parameters only by increasing the catalytic activity of the catalyst used.

An effective catalyst for solid oxide fuel cells should have a developed surface, high catalytic activity at operating temperatures, and good adhesion to the surface of the solid electrolyte [12]. In mass production of the solid oxide fuel cells, the catalyst in the form of fine powder is applied to the solid electrolyte followed by sintering and at temperatures below the melting point of the catalyst, which does not provide good adhesion of the catalyst to the electrolyte surface. One of the main problems of this technology is the difficulty of even distributing the catalyst powder over the electrolyte surface [13]. It leads to uneven catalytic activity and, as a result, a reduction in the specific power of the solid oxide fuel cell. To date, the production of fuel cells uses less such methods as plasma deposition of the catalyst and spraying it in vacuum [14]. Plasma spraying has a relatively high productivity, but is inferior to the method of spraying the catalyst by the uniformity of the vacuum when the catalyst is applied to the surface of the solid electrolyte and does not allow to obtain chemically pure catalysts [15]. To ensure efficient current removal of the generated electricity, a thermally stable silver grid covered with a ceramic capping layer is used in fuel cells [16].

2. Methodology (Method and tools active technological control of process synthesis of catalysts)

Next, we will consider a method of vacuum deposition of a catalyst, which allows to ensure maximum uniformity of chemical purity of catalyst application on the surface of a solid electrolyte.

While spraying substances in a vacuum, there are three main types of film growth: islet, layer-by-layer and mixed. Film growth is influenced by many factors. It is known that a minimal variation in the parameters of the synthesized thin films when sprayed in vacuum can be achieved only using atomic smooth surfaces.

In order to ensure high catalyst activity, it must have a maximum specific surface area that can only be provided by an isolated catalyst structure. The process of islet catalyst growth during vacuum deposition runs in two stages: (1) formation of clusters consisting of two or more atoms on the substrate surface and (2) their subsequent growth. During the spraying process, when the two atoms interact with each other, a chemical bond is formed between them. As a result they remain longer on the surface of the substrate, and the next atom from the molecular stream has time to join them. Thus, a cluster is formed that continues to grow, adding new atoms and combining smaller clusters. Clusters of adsorbed atoms are more linked by molecular forces to the substrate than individual atoms, and tend to grow further due to the entry of atoms from the molecular stream. Furthermore, the addition of atoms also comes from neighboring smaller clusters. As the spraying continues, a network of clusters is formed on the surface of the substrate. These clusters, when the spraying continues, are fused into a continuous film.
When atoms are combined into clusters, their quantum properties are revealed through electro physical parameters of the formed cluster structure (capacitance, resistance, etc.), which can be measured by standard measuring devices. The main idea of the proposed method of active process control of catalyst synthesis is measurement of electro physical parameters (capacitance and resistance) of synthesized structure of islet catalyst and control in real time of process for obtaining catalyst with specified parameters.

Ceramic plates of solid oxide electrolyte are placed at preset distance from catalyst evaporator to implement proposed method. A first control sample is placed near the ceramic plates of the solid oxide electrolyte. The control sample consists of ceramic plate of solid oxide electrolyte with primary measuring transducers (PMTs) located on its surface. PMTs are made by spraying conductive material onto a ceramic plate through a stencil or by photolithography. Structurally, the PMT is made in the form of two groups of conductive electrodes of the inter-digital structure (figure 1a). The electrodes of the first group of PMT1 are made with lattice period \(d_1\), determined by calculation taking into account final size of catalyst clusters. The electrodes of the second group of PMT2 are made with lattice period \(d_2\), determined depending on final size of islet catalyst. By means of PMT1, PMT2, topology of synthesized island catalyst is controlled by measurement of capacitance and resistance between electrodes both at stage of formation of catalyst clusters and at stage of their subsequent growth for achievement of specified parameters by catalyst.

Preliminary experiments had revealed that when the catalyst is sprayed in the interelectrode space of the PMT and, thus, on the surface of the solid electrolyte, an islet structure of the catalyst is formed, the growth of which can be conditionally divided into three stages (figure 1b). At the first stage clusters are massively formed from catalyst substance, in the second stage clusters grow, in the third stage clusters merge to form island catalyst. If spraying is not stopped in the third step, the island catalyst is fused into a continuous film, which is unacceptable in this method.

In order to avoid mass fusion of the islet catalyst into a continuous film, the method proposed provides for the installation of a second control sample, identical to the first one, but 20-30% closer to the source of evaporation of the catalyst than the distance from the first control sample to the evaporator. This arrangement of the second control sample makes it possible to control a more dynamic process of growth of catalyst islands as compared to the process on the first control sample and thus on the surface of the solid electrolyte. This allows complete eliminating of mass fusion of islands on them, i.e. to eliminate defect in the production of solid oxide fuel cells.
The process of island catalyst synthesis is divided into several main stages. In the first stage of spraying (figure 2) clusters of catalyst substance are formed. And in order to increase the number of them, ceramic plates of solid oxide electrolyte and control samples are cooled to temperature in the range from 0 to -50°C depending on the catalyst type and the surface roughness of solid oxide electrolyte. During spraying the capacitance and resistance on the first and the second control samples of PMT1 are measured. The first spraying step is completed when the change in resistance and capacitance on PMT1 reaches steady state (areas A and B) in figure 2, indicating that the number of catalyst clusters has stopped growing.

At the second stage (figure 2) of the technological process, electrodes of fuel cells are heated to temperature in the range of 100-200°C to ensure uniformity of island catalyst growth and improve adhesion of catalyst to surface of solid oxide electrolyte. Then catalyst spraying is continued, and capacity and resistance of the PMT2 of the second control sample are measured. When the maximum capacitance at the PMT2 of the first control sample is reached, or when there is a sharp drop in resistance at the PMT2 of the second control sample, the catalyst spraying process is completed.

3. Experiments to verify the proposed method
The functional diagram of the device implementing the proposed method is presented (figure 3). As the basis of the device there were used a vacuum spraying unit UVN-71 and a developed microprocessor system for monitoring and controlling the process of spraying island catalyst.
Figure 3. Functional diagram of the device implementing the method of active monitoring and control of the catalyst synthesis process: 1 - thermostat; 2 - a ceramic plate holder of a solid oxide electrolyte; 3 - the first control sample; 4 - the second control sample; 5 - electromechanical gate; 6 - substance evaporator; 7 - microprocessor control system.

The device (figure 3) is a software and hardware complex, in which the values of resistance and capacitance of the formed catalyst structure, as well as the main parameters of the technological process (evaporator power, temperature of ceramic plates), measured by all PMT, are used as data for the control program. It implies the use of the boundary conditions and film growth rate values calculated according to mathematical model.

This device works as follows. Digital signals from the first (3) and the second (4) control samples come into the microprocessor control system (7). The microprocessor system (7) sends the control signals to the thermostat (1) to maintain a preset temperature of the ceramic plates of the solid oxide electrolyte (2) and the control samples (3), (4). The information from the PMT of the first and second control samples is processed in real time to determine the stages of the catalyst deposition process according to a given algorithm in the control program. Based on the results obtained during processing of the input information from the PMT, the microprocessor system outputs signals to the electromechanical gate (5) to stop the molecular flows of the evaporated catalyst substance to suspend or completely block the spraying process, and also controls the power of the evaporator of substances (6).

The synthesis of the initial powder of the YSZ system was carried out by chemical precipitation of aqueous solutions of salts of the corresponding metals. ZrO(NO$_3$)$_2$$\cdot$4H$_2$O and Y(COOCH$_3$)$_3$$\cdot$4H$_2$O were used as initial reagents [17]. The amount of yttrium acetic acid corresponded to the molar concentration of yttrium oxide of 8% in zirconium oxide. Hexamethylenetetramine was added to the salt solution in an amount of 1:1. The resulting solution 100 ml was placed in a 50 W ultrasonic cleaner for 15 minutes at a temperature of 90 °C. The resulting suspension was then deposited in a centrifuge (RCF 240). The resulting precipitate was then washed in a mixture of distilled water with isopropanol and dried at a gradual temperature increase from 25 to 190 °C. To remove hexamethylenetetramine residues and start forming the necessary phase composition, the mixture was annealed in a muffle furnace at a temperature of 600°C for 20 minutes, and then the annealed powder was thoroughly ground. The resulting powder was passed through a plasmatron according to the method described in work [18]. The resulting powder was compacted at a pressure of 250 MPa by cold isostatic pressing. Sintering powder was carried out at a temperature of 1500 °C for 1 hour in a vacuum furnace.

To test the effectiveness of the proposed method, 30 YSZ ceramic plates were manufactured. LaCoO$_3$ [19] powder was used for the cathode material and NiO [20] for the anode material. For
production of the first batch of 10 fuel cells the proposed method of active monitoring and control of the process of island catalyst synthesis on ceramic plates YSZ was used. The second batch of 10 pieces was manufactured using traditional powder technology by screen printing with a paste of anode (NiO) and cathode (LaCoO₃) material on the surface of ceramic plates YSZ and subsequent sintering.

Resistance to thermal cycling of two batches of fuel cells with simultaneous measurement of their volt-ampere characteristics has been examined. For this purpose, 50 heat cycles of heating and cooling were carried out in the muffle furnace. The test fuel cells were heated to 700°C at an average rate of 20°C/min, the fuel cells were kept at that temperature for 10 minutes, then the heating was turned off and oxygen and hydrogen were supplied. Next, after setting the power generation mode, the output power of the fuel cell was measured, then the fuel cells were cooled to 100 °C at an average speed of 20°C/min, and the cycle was repeated.

The graph of power change of two fuel cell batches during 50 heating-cooling cycles is shown in figure 4.

![Figure 4. Fuel cell power change dependence during thermal cycling: 1 – fuel cell manufactured using active monitoring and control method; 2 - fuel cell manufactured without active control.](image)

The analysis of the power change dependence of the fuel cells during thermal cycling has revealed that the fuel cells made using the proposed method do not actually reduce their power within 24 cycles of thermal cycling, presumably because of better adhesion of the catalyst to the surface of the solid oxide electrolyte. While in fuel cells produced without using the proposed method, the power loss occurs almost from the beginning of the thermal cycling, with a sharp power loss of up to 7 cycles, presumably due to partial precipitation of the catalyst. On the basis of the data obtained, it can be concluded that fuel cells of the first batch manufactured using the proposed method produce a higher power by 16% at the beginning and after 50 cycles of thermal cycling by 40-50% than fuel cells of the second batch, and, thus, are more preferable for using in low-power and portable equipment.

4. Conclusion

The method and the microprocessor measurement and control system implementing it, allow real-time control of the process of synthesis of the island catalyst on the surface of the solid electrolyte by measuring the capacitance and resistance of the synthesized island catalyst. The division of the spraying process into two stages allowed increasing the number of catalyst clusters in the first stage, resulting in subsequent synthesis of the catalyst with a maximum specific area. At the second stage, due to heating of solid electrolyte surface during spraying uniformity of island catalyst growth
increases as well as its adhesion to solid electrolyte surface. This allowed the creation of fuel cells with increased specific power and extended service life.

Thus, the pilot studies have shown the effectiveness of the method of active control of catalyst synthesis on the surface of a solid electrolyte, which can be used in the development of advanced fuel cells with smaller weight and size parameters and increased operational resource.

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