Research project objectives/Research hypothesis

Under the conditions of our modern society, where the energy needs grows daily the matter of alternative energy sources raises rapidly. The fuel cells have become one of the fastest developing technologies of recent years. The high efficiency of the utilization of fuel energy and elimination or considerable reduction of toxic exhaust gases emissions constitutes their attractiveness as alternative sources of electricity. Moreover, polymer fuel cell systems are widely recognized as the most promising concept for innovative future energy, mostly due to their ecological character. However, the commercialization of fuel cell technology is still a great challenge, mainly due to the slow kinetics of the oxygen reduction reaction (ORR) at the cathode and the high cost of Pt-based cathode catalysts. Therefore, the design and synthesis of new type, non-noble metal catalysts are one of the most important goals, in context of the fuel cell spreading.

The proposed research project is aimed at the design and investigation of the physical and chemical properties of an innovative type of electrocatalysts for ORR. The main **scientific objective** of the project is to reveal the mechanism of the ORR on the carbon supported spinel electrocatalysts, and to understand the mutual interactions between the oxides and doped carbon support moieties. Particularly, synergetic effect of spinel redox properties and basicity/acidity of the support will be examined in detail. During catalytic reduction of oxygen, particularly when platinum group metal–free (PGM-free) catalyst is used, some amount H_2O_2 of (2ē reduction pathway) is always produced. The hydrogen peroxide can be than decomposed to radical oxygen species (ROS), which are destructive for both carbon support and polymer electrolyte membrane (PEM) used in fuel cell. So, we propose to add to the Sp/HE-C system **inorganic catalase like catalyst** which will decompose H_2O_2 into the dioxygen O_2. A secondary goal is to clarify the role of the faceting and spinel distribution with the respect to its electrochemical activity. To achieve the project objectives systematic investigation of the catalysts redox properties, zeta potential and identification of intermediate species will be accomplished. The catalysts will be based on the transition metal oxides (spinel structure) supported on carbon modified by simultaneously doping with heteroelements (HE) such as: N, S, B, P, Se. It is assumed that, the enhanced activity of the proposed materials is related to the simultaneous effect of several factors. The first one is associated with the spinel composition, size and distribution of nanoparticles as well as theirs morphology. The second group of factors include properties of modified carbon, and the third group is related to the presence of transition metals in the form of nanoparticles in carbon lattice. As a **research hypothesis** we assume that the nature of the **carbon carrier plays a triple role** in the ORR activity, determining dispersion and faceting of the spinel nanoparticles, as well as the extent of the undesired 2ē reduction pathway, controlled by the fraction of an amorphous component. Additionally we made an assumption that oxygen reduction in an aqueous medium takes place according to an **intermolecular electroprotic mechanism** (coupled electron and proton transfer) joined with the capture of the corresponding ionic species by the oxide surface.

Research methods used/methodology

The studies will focus on the explanation of synergetic effect of spinel redox properties and modified carbon supports on the catalytic activity and long-term stability of the catalysts. The project consists of three interconnected parts - synthesis, physicochemical characterization and catalytic activity tests. In the first step, precursors will be obtained by using a modified approach, in which a new heteroatoms-containing organic precursor will be synthesized in the reaction of oxidative polymerization of heterocyclic species which ensures homogenous HE distribution and simultaneously in situ incorporation of nanoparticles of transition metals in the carbon lattice. Synthesis of spinel on modified carbon support will lead to obtaining of active and stable catalysts with optimized structure and morphology. In the second step, the studies will focus on physicochemical characterization of materials by using the modern spectroscopic and microscopic methods, which will allow detailed characterization of the materials and the determination of the active sites. The electrochemical tests will be used to establish the activity of the catalysts and to resolve the possible mechanism of ORR. Finally, the most promising catalysts will be tested in the model fuel cell setup in order to determine their effectiveness and long-term stability.

Effect of the expected results on development of science, civilization, society

The clarification of the processes occurring during simultaneous incorporation of the HA and M will be significant from scientific and practical point of view. This will allow to elaborate a new composite, non-noble metal catalyst for ORR. The proposed project will contribute to understanding of the role of oxide nanoparticles faceting and their distribution on the surface of modified carbon for the formation of electrocatalytically active centers. Development of affordable, effective and stable catalyst for fuel cells will significantly contribute to the dissemination of fuel cells as a power source for mobile applications. Moreover, the research is critical for the solution of the ecological problems, as well as for a wide commercialization of fuel cells as green and sustainable energy sources, and will significantly decrease the pollution caused by burning of fossil fuels.