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Challenges of Fuel Cell Technologies for the Needs of the Energy Transition to a Zero-carbon Technology

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Abstract. The study focuses on the challenges of implementing fuel cell technologies and materials to achieve efficient use of green hydrogen and zero CO_2 emissions. It is shown that only identifying the optimal parameters for each fuel cell component and technology and testing the system will help achieve the planned output-specific power. The thorough structure optimization of the membrane-electrode complex and testing in actual operating conditions will accelerate the implementation of fuel cell technologies. An example of structural optimization and improvement of catalytic activity of electrodes and electrolytes is shown. The current density of 0.36 $\mu A/cm^2$ was obtained at a voltage of 0.6 V and a temperature of 500 °C for the fuel cell with 75–80 μm thick ZnO electrolyte and without membrane electrode assembly optimization. It is shown that the fuel cell electrodes' catalytic activity depends on the modeling profile and structure of the catalytic layer, which was verified by testing in real fuel cell operating conditions.

Keywords: fuel cells, electrolysis cell, material science, hydrogen energy, decarbonization.

1 Introduction

The modern world is moving away from a fossil fuel-based economy, as CO_2 emissions are at the root of climate change and the critical environmental situation. There is an urgent need to introduce environmentally friendly fuel sources that use fuel cells and green hydrogen technologies, which allows the fuel cell system to enter the market as zero-emission technologies [1]. The significant event in the world is the first implemented hydrogen law, which entered into force on February 5, 2021, in South Korea to promote the development of the hydrogen economy. The law has become the main piece of legislation governing the hydrogen industry, while the RES (renewable energy source) law will be used in matters not covered by the fundamental law. Currently, in Ukraine, the main steps are forming the hydrogen strategy and implementing strategic research works in the scientific field through fundamental research projects of NAS of Ukraine [2]. The work is devoted to studying the peculiarities of the development of fuel and cell technologies in decarbonization and transition to a zero-emission economy, which consists of developing fuel and cell technologies and achieving maximum electrical efficiency of electrochemical conversion of 1 kg of hydrogen.

2 Literature Review

With a growing population and, as a result, growing energy needs, environmental problems, and climate change are becoming the challenges for our other existence [3].

According to the World Health Organization, every 9 out of 10 people breathe polluted air. This means that almost 91 % of the world's population does not have access to clean air, and high levels of pollutants cause the deaths of more than 8 million people annually [4, 5].

According to the AQLI (the air quality life index), polluted air is the greatest threat to reducing life expectancy, compared to smoking, alcohol dependence, polluted water consumption, road accidents, diseases, and terrorism. It is becoming clear that implementing policies to combat pollution can allow people to live longer and healthier today. The UN Framework Convention on Climate Change, to which Ukraine is a party, aims to preserve the environment by stabilizing greenhouse gas concentrations in the atmosphere at a level that would not allow dangerous anthropogenic impacts on the climate system (Law No. 435/96-VR dated by 29.10.96, BBP, 1996, No. 50, p. 277).

The main steps to overcome this global problem are the energy transition to clean energy sources and decarbonization processes (Paris Agreement from 2015 adopted under the UN Framework Convention on Climate Change to avoid dangerous climate change by limiting global warming to well below 2 °C and pursuing efforts to limit it to 1.5 °C). Reducing fossil fuel consumption and switching to renewable energy sources are steps in the global decarbonization agenda and meet the goals of sustainable development [6].

– goal 7: ensure access to affordable, reliable, sustainable, and modern energy for all;

– goal 12: ensure sustainable consumption and production patterns;

– goal 13: Take urgent action to combat climate change and its impacts.

The main stages of decarbonization include 3 levels of energy transition:

– an increase of efficiency (energy efficiency) - 1st level of decarbonization, get more power from fuel;

– hybridization/fuel transition – 2nd level of decarbonization, use of low carbon fuel;

– deep decarbonization – 3rd of decarbonization, hydrogen fuel, and carbon capture technologies are key factors in “zero” CO_2 emissions.

Implementation of the first level of decarbonization is a set of measures aimed at reducing energy consumption by transport, buildings, and factories. Examples include improving the energy efficiency of buildings, reducing the fuel consumption of vehicles, and optimizing fuel supply. Everything that will contribute at all levels and in all possible ways to reduce energy consumption by the population and any production aspect.

To implement the second level of decarbonization, the international community, especially developed countries, is setting a time frame until 2030. There is a gradual transition from natural gas to biomethane, distributed through the existing gas infrastructure. It is also projected to increase the share of renewable energy and develop infrastructure for hydrogen fuel. The following main measures can be identified to ensure the 2nd level of decarbonization [6].

The transition from the second level of decarbonization to the final level is limited to 2030–2050. This period is characterized by hydrogen fuel, CO_2 capture, and hydrogen and CO_2 storage technologies and has the potential for deeper decarbonization of fossil fuels. These technologies should significantly change the ability of the oil and gas industry to reduce carbon emissions. It is also planned to significantly increase the share of renewable electricity for green hydrogen production, which will come directly to the infrastructure of the distribution network. The transition between decarbonization levels 2 and 3 is schematically shown in Figure 1.

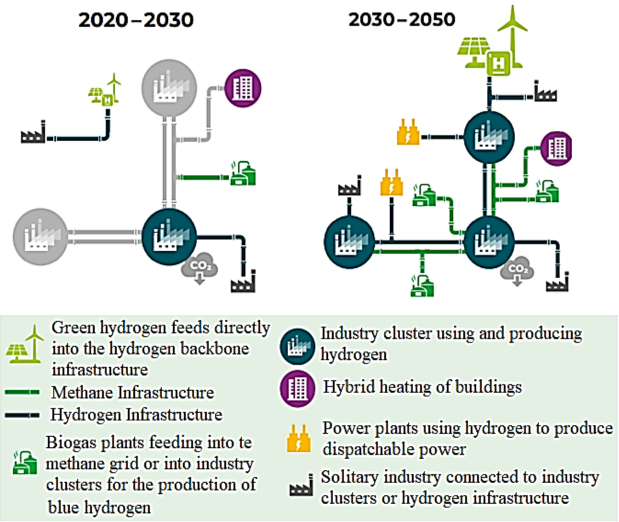

Figure 1 – Development of energy infrastructure in the periods 2020-2050 in terms of decarbonization steps, adapted from [7]

The main advantage of using hydrogen as a fuel is the significant compensation during intermittent energy production from renewable energy sources, which consists of the production and storage of hydrogen (closed cycle of green energy) [8]. Simultaneously, the primary purpose of using hydrogen as a carrier of clean environmental energy is the production of electricity and heat.

Currently, hydrogen is produced by steam reforming from natural gas, although biomethane can significantly reduce carbon emissions during hydrogen production (blue hydrogen). Pure hydrogen production is possible using the reverse mode of fuel cells (FCs) or electrolytic fuel cells.

FC is the most energy-efficient device for generating electricity, which consumes hydrogen as a fuel and oxygen (from the air) as an oxidant. Such devices can be used in all areas of electricity consumption with distributed stationary production of electricity in heavy vehicles and cars. Therefore, issues related to the operation of such energy sources are relevant today.

That is why the implementation of available and known chemical and electrochemical reactions for energy production by using FCs, when chemical energy contained in fuels (hydrocarbons or pure hydrogen) directly and in an energy-efficient way converts into electrical and thermal energy, gives priority in current conditions of planetary pollution over fossil fuel combustion.

The transition from a fossil energy economy to a hydrogen-based economy, if the technologies are available, requires the widespread use of renewable energy sources, including hydrogen production and storage to stabilize electricity supply by regulating renewable energy intermittent; for the production and storage of hydrogen (the so-called buffer to increase the stability of the energy system of a country or region) [9].

One of the most straightforward production processes of pure hydrogen is its production from water by electrolysis, which can be carried out using electricity from other renewable energy sources, such as wind energy, solar energy, or water energy. In such cases, there are two additional benefits in obtaining hydrogen. The first one is that hydrogen can be used to supplement and adjust electricity generation (so-called intermittent production) when there is a shortage of water, wind, sun, or ocean activity, but there is an electricity demand. Hydrogen, which is already extracted and accumulated, can be easily converted into electricity by FCs (Figure 2). Another valuable property of hydrogen accumulation manifests itself in increasing the resilience of the entire energy system of a country or region, stabilizing the regional electricity distribution network.

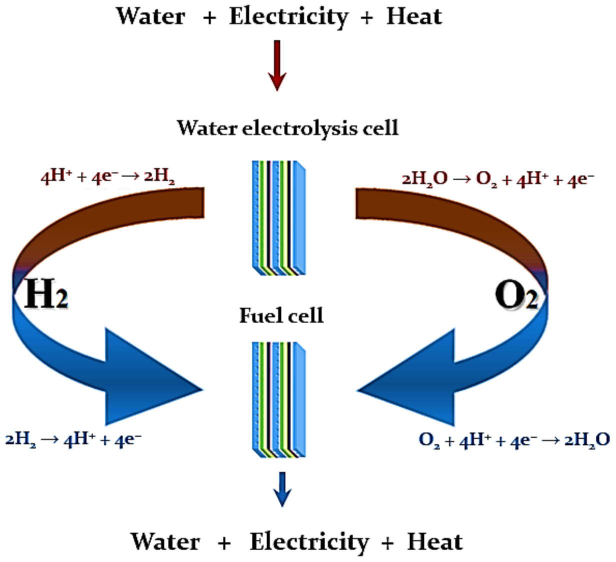

Figure 2 – Process of electrochemical conversion of hydrogen fuel and oxidant to water in the fuel cell system and components of the battery of two fuel cells

Finally, and most importantly, it is clean energy that meets all the possible demands of decarbonization to improve social and environmental needs, and therefore the goals of sustainable development, to which Ukraine has joined. Decarbonization reduces or eliminates carbon dioxide from the energy production process. According to the World Economic Forum, complete decarbonization of our energy systems is the only solution to stabilize the climate. Thus, in practice, achieving zero emissions requires a transition to clean energy sources and a complete transition from fossil fuels to electricity from clean sources.

The most efficient technology for obtaining hydrogen is electrolysis (water electrolysis cell), and the reverse mode of conversion of hydrogen (with oxidant) into water is provided by highly efficient fuel cell technology.

A fuel cell is a device that directly converts chemical energy into electricity by electrochemical oxidation of fuel (e.g., hydrogen, methanol). The operation principle of a fuel cell stack and its constituent elements is schematically shown in Figure 3.

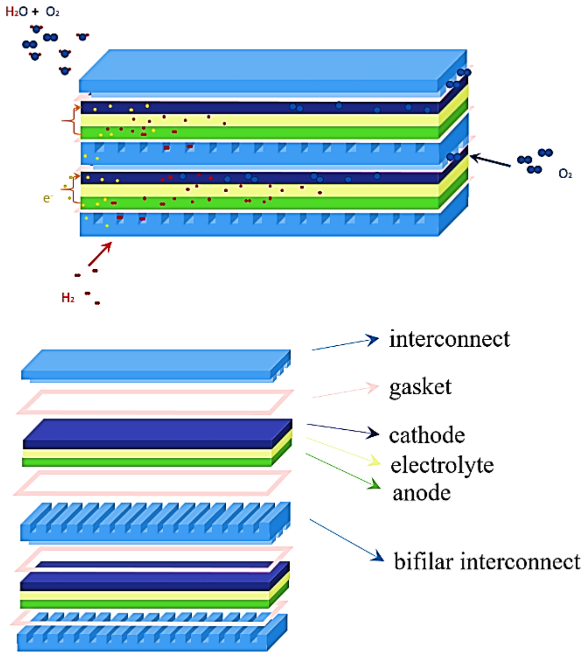

Figure 3 – Electrochemical conversion of hydrogen fuel and oxygen to water in the fuel cell system and components of the stack of two cells.

The fuel cell consists of an electrolyte layer located between two porous electrodes (anode and cathode). Hydrogen and oxygen molecules enter the porous structure of the anode and cathode, respectively, through gas channels on the plate (interconnect), connected by a dense electrolyte material. The anode, electrolyte, and cathode form a membrane-electrode complex of the fuel cell, in which the electrochemical process takes place. Hydrogen molecules on the catalytic component of the anode material dissociate into protons that pass through the anode, which contains the electrolyte material, and the electrolyte to the cathode, which also contains electrolyte material, and electrons along the outer circuit and electrical conductor (anode and cathode material) transfer to the cathode. As a result of the oxygen reduction reaction on the catalytic material of the cathode, water is formed. This type of fuel cell is proton-conducting, and the main characteristic of the electrolyte material is the proton conductivity.

In terms of electrolytes, FCs can be classified into many types, such as alkaline (usually KOH) FCs (AFCs), phosphate FCs (PAFCs), molten carbonate FCs (MCFCs), where a mixture of Li_2CO_3 and K_2CO_3 is used, solid oxide or ceramic FCs (SOFCs, commercial SOFCs usually uses yttrium stabilized zirconia electrolyte) and proton-exchange membrane FCs (PEMFCs). SOFCs and PEMFCs can be divided by their operating temperature: high-temperature (800–1 000 °C for SOFCs with a ceramic electrolyte and 110–180 °C for HTPEMFCs with a polymer electrolyte) and low-temperature (500–600 °C for LTSOFCs and 40–80 °C for PEMFCs) fuel cells. Low-temperature PEMFCs are most widely used due to the low operating temperature of the electrolyte (and a system as a whole), but in Ukraine, the research is focused on SOFCs. In terms of application for transport and mobile devices, the advantages of PEMFCs are low operating temperature, high specific power, fast start, high efficiency, easy and safe operation. The comparison of the main FC types that have the most significant potential for implementation or have already been implemented (PEMFC) is presented in Table 1.

Table 1 – Comparison of different types of fuel cells

Fuel cell	Membrane	Fuel	T, ºC	Efficiency, %	Charge carrier
PEM	Nafion	H_2 MeOH	60–80	40–60	H^+
HT PEM	PBI	H_2 MeOH	110–180	50–60	H^+
SOFC	$(Y_2O_3)_x(ZrO_2)_{1-x}$	CH_4 MeOH H_2	800–1 000	55–65	O^{2-}
LT SOFC	CeO_2-based	CH_4 MeOH H_2	550–600	55–65	O^{2-}

Among the energy conversion devices that use hydrogen, FC technology occupies a unique place. Hydrogen-containing methanol (MeOH) fuel is available for widespread use without significant infrastructure costs, which is an ideal hydrogen carrier for transportation because it is liquid at room temperature and ambient pressure. The hydrogen release from the methanol molecule’s bound state is more accessible than in other liquid fuels. Moreover, methanol fuel does not contain sulfur, which is harmful to FCs, and the high ratio of hydrogen to carbon in methanol makes it a promising fuel for the hydrogen economy. Methanol is an example of hydrocarbon-containing fuel for the transition period to achieve an economy with zero CO_2 emissions.

Electrolytic FCs can be similarly divided according to their operation principle and characteristics. As for SOFC, the high temperatures (700–900 °C) of the ceramic electrolysis cell (SOEC) provide high efficiency, namely up to 98 %. There are other electrolyze technologies of this type on the market [10]. Like the fuel cells, electrolyzers can be divided by the type of electrolyte. In the case of the alkaline electrolyzer cell (AEC), the electrolyte is a liquid solution of NaOH or KOH, so that OH^- becomes a conductor of ionic charges. This technology uses carbon, transition, or precious metals as catalytically active materials, electrodes, and connectors and operates at temperatures of 40–90 °C. Electrolyser based on proton exchange membrane (FC with polymer electrolyte) has an electrolyte consisting of hydrated polymer membrane and conducts protons through the membrane. The electrode mainly contains carbon, platinum, and iridium-based materials. The operating temperature of the electrolyzer ranges from 20 °C to 150 °C. The main characteristics of the most common electrolyzers are summarized in Table 2.

Table 2 – Comparison of two electrolyzer cell technology

Electrolysis cell type	PEMWE	SOEC
Electrolyte	PEM	Ceramics
Charge carrier	H^+, H_3O^+	O^{2-}
Cathode reaction	$2H^+ + 2e^- \rightarrow H_2$	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$
Anode reaction	$H_2O \rightarrow ½O_2 +$ $+ 2H^+ + 2e^-$	$O^{2-} \rightarrow ½O_2 + 2e^-$
Electrode materials	C	Ceramics
Catalytic materials	Pt, Ir	Ni, LSM, LSCF
Interconnect	Carbon / metal	Modification of stainless steel/metal ceramics
Operation temp., ºC	20–150	600–900

The electrochemical process of the closed cycle of green hydrogen (Figure 2) takes place in the membrane electrode assembly of the fuel or electrolysis cells, namely in the anode-electrolyte-cathode structure (Figure 3). It is a process that consists of producing H_2 as an energy source from the splitting of water, and the subsequent use of such energy, which relies on four elementary reactions, i.e., hydrogen evolution reaction (HER), hydrogen oxidation reaction (HOR), oxygen evolution reaction (OER) and oxygen reduction reaction (ORR).

The main goal is to recommend systematic protocols for measuring the activity of these four reactions and reference actions in real electrochemical transformation systems, which is critical to facilitate research and development of new materials with high activity and stability in FC and electrolytic FC electrodes.

Detailed information on the electrochemical tuning of FCs and electrolysis FCs, measurement, and analysis of data used to quantify the processes of reverse systems in acidic and basic solutions, are given as examples of the latest specific and mass activity of catalytic materials. Experiments should be performed correctly, and general recommendations for appropriate reactions should be provided, including cell design, electrode structure, selection of catalytic and electrolyte materials. It is essential to develop experimental protocols, including data collection and processing, such as ohmic and background correction and surface evaluation of catalytic materials, materials with different electrolyte conductivity, the practicality of tests, and comparison of different classes of materials for hydrogen energy. Finally, it is necessary to qualitatively assess some modern catalysts’ specific and mass activity to facilitate comparison and interpretation of catalyst activity for these four reactions in different laboratories because different types of fuel cells require different operating temperatures. Figure 4 schematically illustrates the composition of materials included in the membrane electrode assembly.

Catalytically active materials are needed to increase the kinetics of these reactions and thus meet the practical demand to increase the efficiency of electrochemical conversion in FC and electrolytic FC and reduce energy loss during the entire cycle. Scientists are trying to discover and establish the principles of designing catalysts with more significant activity through systematic experimental and computational studies [11–13], some of them focus on increasing the mass-specific surface area of catalytically active materials by designing and creating new structures of catalytic layers/electrodes [14, 15].

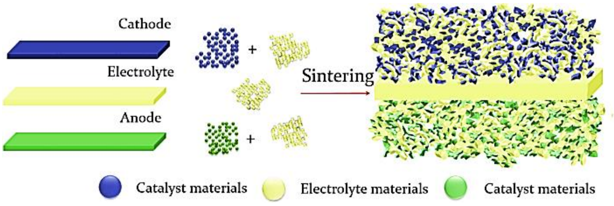

Figure 4 – Materials for the membrane electrode assembly (anode-electrolyte-cathode)

Understanding the mechanisms of reactions, obtaining the maximum possible values of specific activity of catalytic materials, and identifying active sites for catalyzing URFC (unitized reversible fuel cell) processes are studied systematically. The results are often associated with a clear definition of material surfaces, such as single crystal faces [16, 17]. The development of highly active electrocatalysts for practical use is associated with specific methodologies of electrochemical measurements [18, 19] and comparative evaluation with modern electrocatalysts [20]. Unfortunately, today a careful comparison of such studies in real FC devices and electrolytic FCs in most cases only allows assessing the performance of the whole device. Unfortunately, there are often cases when electrocatalytic material was unpromising, although electrochemical tests for electrocatalysis were successful. In the case of high-temperature SOFCs, precious metals are not used as catalytic materials, so the catalytic material in the structure of the electrodes acts as an electrical conductor.

A complex electrochemical process characterizes the fuel cell system with one type of conductivity, while each component of the fuel cell should meet specific requirements, meeting which does not always guarantee high efficiency in actual conditions [21, 22].

Therefore, it is reasonable to assume that in the case of analysis of the process kinetics at each of the FC electrodes or the efficiency of an electrochemical reaction in the system with mixed conductivity, the task becomes much more complex. Thus, it is obvious to perform structural optimization of each element of the fuel or electrolysis cell and test new materials and structures in real conditions of electrochemical transformation.

An essential characteristic for electrolyte materials is the ionic conductivity of materials, which in most cases is regulated by nanostructural or morphological features, such as the shape and size of ionic domains and their interaction. Therefore, oscillations either in the nanostructure/orientation or in the transport mechanism can change the activation energy of conductivity. Recent studies have shown that the nanostructure and morphology of the thin layers of Nafion electrolyte, the most commercialized membrane for PEMFC, differ from the thick Nafion layers [23]. It is noted that the conductivity of the thin Nafion layers becomes dependent on the humidity, which is not observed for thick membranes.

One of the main reasons is the high interfacial area ratio and volume of thin layers. As a result, the substrate causes interfacial and configurational effects when the morphology and properties of thin films predominate [24].

Ceramics with ionic conductivity are used as electrolytes in high-temperature and low-temperature SOFCs. Thus, high ionic conductivity (more than 0.1 S/cm), density, mechanical properties, minimum thickness, stability in real conditions of electrochemical reactions are required. The oxygen ion conductivity in ZrO_2- and CeO_2-based ceramics, commercialized in SOFC technology, is well studied and governed by grain boundary and defects concentration (typically dislocations or differently oriented domains) [25]. However, using semiconductor materials leads to more complicated kinetics processes and mixed conductivity when the electrolyte has both ion and proton conductivity [26–28].

A breakthrough in micro-energy technologies is required to cover the increasing demand for embedded, personal, or local use of power. Due to their miniaturization capabilities, solid-state energy devices are promising candidates to play a significant role in this new era. However, improving their performance while downscaling their size can only be achieved by looking for disruptive concepts in materials capabilities [29].

Achieving the requirements for electrolyte materials and FC electrodes should ensure high process efficiency, namely the high specific power of the fuel system [30], which is currently not achieved in real conditions.

3 Research Methodology

The morphology and structure of the ZnO-based electrolyte were examined using a scanning electron microscope (SEM) Superprobe 733 (JEOL, Japan).

The chemical composition and structure of the powders were determined by spectral analysis and X-ray phase analysis.

For the morphological investigation of the catalytic layer, a scanning electron microscope (SEM) TESCAN MIRA3 was used. The measurement was carried out in the secondary-electron-mode using primary electrons with 30 keV energy.

The porosity of the samples was measured by hydrostatic weighing.

The electrolyte tests in real operation conditions of the fuel cell were carried out on a new stand for studying the efficiency of materials for hydrogen energy (IPM NAS of

Ukraine). Hydrogen and oxygen were obtained from a polymer-type electrolysis battery. The anode and cathode of the fuel cell were formed using a platinum-rhodium grid (12217, AlfaAesar). The temperature range was set from room temperature to 650 °C.

To form a multilayered electrolyte with a thickness up to 80 µm, a mixture of ZnO nanopowder and polymer with the ratio of 90:10 and 92:8 was used, which was preliminarily homogenized for 4–8 hours in 30 % aqueous-alcohol solution (isopropanol and deionized water). The mass fraction of solid components in the solution was 1 mg per 10 ml of solution.

4 Results and Discussion

4.1 Chemical reactions

The overall chemical reaction in the fuel cell is characterized as follows:

$$1\,kg\,H_2 + 8\,kg\,O_2 = 9\,kg\,H_2O + \approx 39\,kW \cdot h + Q \quad (1)$$

According to the state-of-the-art technology and materials, the generation of 39 kW·h of electricity by SOFCs with an efficiency of 85%, where the rest is released as heat, is achievable. While the overall efficiency of PEMFCs reaches 70 %. Note that the thermodynamic efficiency calculated as efficiency from the ratio of Gibbs function for total reaction (1) gave 83 % for ideal FC. That means 39 kW·h value of electrical energy will be much higher.

In the case of the reversed electrochemical reaction, namely electrolysis, the reaction can be written as follows:

$$9\,kg\,H_2O + \approx 39\,kW \cdot h + Q = 1\,kg\,H_2 + 8\,kg\,O_2 \quad (2)$$

PEMWE electrolysis technology has an efficiency of 75–93 %, and the total energy consumption reaches 45–53 kW·h. At the same time, the efficiency of SOEC is higher and reaches 90–98 %. In state-of-the-art production, energy costs for SOEC technology require 34–37 kW·h of electricity and 6–11 kW·h of thermal energy.

To approximately estimate the consumption and price of hydrogen, we present the following data:

1 kW·h PEMWE produces 0.016-0.018 kg/h H_2
1 kW·h SOEC produces 0.022-0.028 kg/h H_2
1 kW·h PEMFC consumes 0.069 kg/h H_2 [31]
1 kW·h SOFC consumes 0.0534 kg/h H_2 [32]

In 2020 the cost of hydrogen varied as follows: 2.50–6.80 USD/kg for green H_2; 1.40–2.40 USD/kg for blue H_2 (biofuel), and 1.00–1.80 USD/kg for gray H_2 (from hydrocarbons).

The strategy for the transition to technologies with zero CO_2 emissions involves using blue and green hydrogen, and fuel cell technologies are at the forefront of different development strategies of many countries (Hydrogen Road Maps). To reach high efficiency (reactions (1)–(2)), scientists are focusing on the development of new materials and improving their properties. However, above all, it is necessary to ensure the efficiency of the whole FC system to achieve better performance for FC materials and complete structural optimization of all fuel cell elements and technologies.

4.2 Structural optimization

According to DOE, the catalytic layer's percentage of catalytically active platinum is less than 50 %. Figure 5 schematically shows the catalytic layer, which consists of platinum particles on a carbon carrier, and schematically shows the catalytic layer in actual FC operation conditions, when the amount of catalytically active material is reduced significantly.

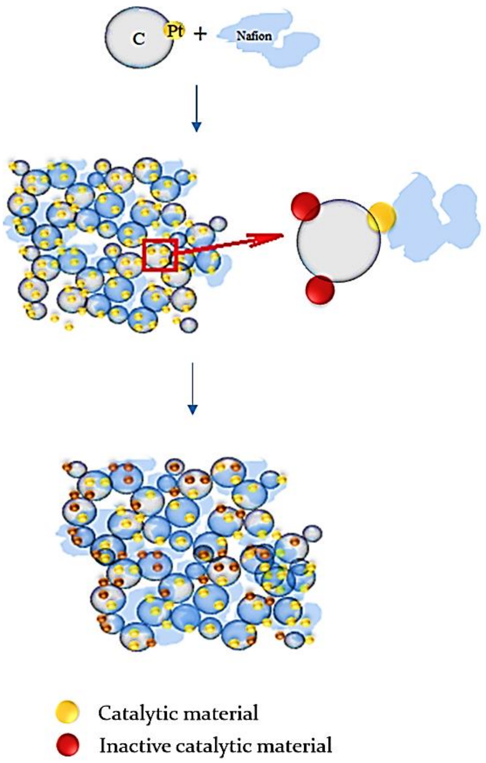

Figure 5 – Catalytic layer of PEMFC: catalytically active Pt (yellow), inactive Pt (brown), carbon (gray), polymer component (Nafion^{TM})

Stable electrochemical conversion on FC electrodes is ensured by a constant flow of semi-cellular redox reactions, which begin on the surface of the catalytic material with constant removal of protons and electrons to the polymer electrolyte (Nafion^{TM}) and electronic conductor (carbon particles). The catalytically active platinum is depicted by a yellow color, while platinum which does not contribute to the efficiency of electrochemical conversion, is depicted by brown color.

The content of one of the components or adding other structural changes to the whole catalytic layer is varied. Therefore the study of FC processes in conditions of low content of catalytically active material is a difficult task with many uncertainties and complexities. Solid platinum

[22] is usually used as a reference for non-Pt systems, especially concerning activity, but it is proven theoretically and experimentally that platinum activity can be significantly improved by doping with other metals. Thus, the efficiency of the modified Pt systems becomes a reference point for implementing hydrogen conversion technology into electricity. In energy conversion devices, weight and efficiency play an important role, and the amount of catalyst in fuel cells for fuel conversion, in general, can be a critical parameter.

The magnetron sputtering was used for the controlled deposition of the catalyst material. To obtain a highly dispersed substance by magnetron sputtering, a surface with high specific area [22]. Usually, the catalytic layer is made of catalytic ink and is applied on the surface of the electrode with the presence or absence of a hydrophobic microporous layer. In our case, the adapted catalytic ink method was used to form a surface with an active support layer for platinum catalyst. For obtaining a standard PEMFC catalyst layer, the catalytic ink contained a catalyst material (catalyst nanoparticles or carbon-supported catalyst nanoparticles), proton-conductor membrane ionomer dispersion, and the aqueous-alcoholic solution used. Since the catalyst material was obtained by magnetron sputtering, the catalyst material was absent in the prepared ink. The microporous layer was formed from a mixture of carbon carrier (nanoparticles of size 20–50 nm), 5 % Nafion ionomer dispersion or polytetrafluoroethylene dispersion, isopropyl alcohol, and water. Figure 6 shows the microporous carbon-based surface and Nafion ionomer images before and after hot pressing. This technique is applied to obtain a sandwich-like catalyst, the details, and parameters described in [33, 34]. Hot pressing is usually used to form a membrane complex of the fuel cell with improved proton conductivity at the interfaces between the membrane and catalytic layers of the anode and cathode.

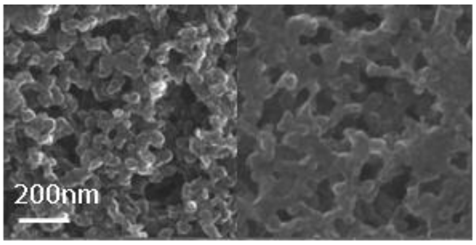

Figure 6 – SEM image of the surface of microporous layer based on carbon nanoparticles and Nafion ionomer (25 %) before and after hot pressing

During the formation of the catalytic layer by magnetron sputtering on this type of surface (Figure 1), the thickness of the deposition film should not exceed 50–60 nm in the case of pure platinum since a further increase in thickness does not increase the fuel cell efficiency [22]. The catalytic layer can be deposited on the surface of the electrode (anode/cathode) or the surface of the membrane during magnetron sputtering. In the latter case, hot pressing is used, and the amount of the active catalyst can be increased during a deposition of a sandwich-like structure of the catalyst material for direct and reverse FC [34]. The catalytic layer is shown in Figure 7. In the near-membrane catalytic layer (Figure 7 a), the catalyst material is deposited by magnetron sputtering on the surface of the microporous layer and transferred to the surface of the membrane by hot pressing. When the catalytic layer is located on the support (Figure 7 b), the catalyst material is deposited by magnetron sputtering on the surface of the microporous layer, which was transferred to the membrane by hot pressing.

Performed studies on the catalytic activity of the anode and cathode materials in real FC operation conditions resulted in developing a layered structure of the anode and cathode with a polymer electrolyte and ultra-low platinum content [21].

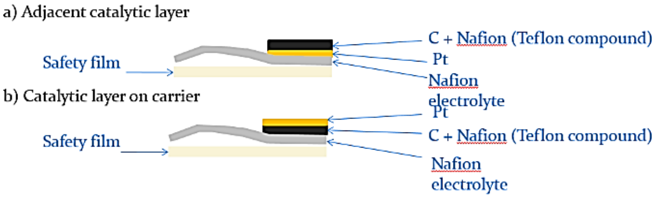

Figure 7 – Model of catalytic layer deposition: a – in-orientation or adjacent catalytic layer; b – top-orientation or catalytic layer on the carrier

The amount of platinum can be reduced to 1–10 μg/cm^2 on the hydrogen electrode (anode) and up to 40–60 μg/cm^2 on the cathode by deposition the catalytic layer on the surface of the electrode with a hydrophobic microporous layer [22]. Further reduction in the amount of the catalyst is possible by carbon doping [35].

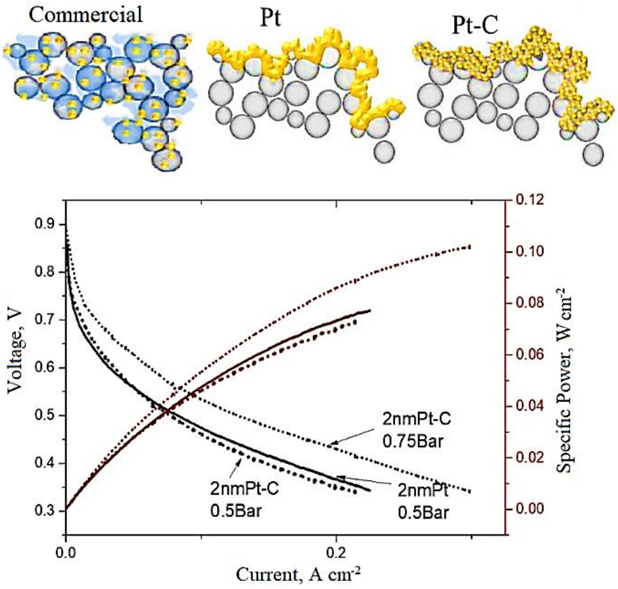

Figure 8 – VA curves for Pt and Pt-C thin films with a thickness of 2 nm on the cathode side of the FC (anode 300 μg/cm^2 Pt, Nafion 212)

Figure 8 also schematically represents the formation of a pure platinum catalytic layer on a carbon carrier and porous structure during the simultaneous deposition of platinum and carbon by magnetron sputtering. By replacing the “bulk” Pt catalytic layer with Pt-C composite, we reduce the amount of Pt in the catalytic layer, while the catalyst dispersion is improved due to the roughness of the surface. The FC tests showed that the samples had almost the same initial characteristic (Figure 8) when the catalyst layer on the cathode was pure Pt and Pt-C (11 % Pt) with an equivalent thickness of 2 nm. However, the porous structure of the Pt-C composite has an advantage in the case of increased pressure inside the FC. The efficiency of the FC increases by only 20–25 % for pure Pt thin films with increasing pressure, and then the efficiency decreases. The evolution of the development of new material is shown in Figure 8 (top).

According to this technique, the content of precious metal in the membrane complex of FC can be significantly reduced without loss of initial characteristics and long-term stability of FC compared to the conventional catalysts on carbon carriers.

The effect of pressure was used to control ionic conductivity in SOFC electrolyte materials based on zinc oxide.

4.3 Structural optimization of electrolyte

Zinc oxide can be used in SOFCs as a primary or alloying material to increase ionic conductivity, reduce sintering temperature, improve the mechanical properties of the electrolyte, and reduce the operating temperature of the cell.

After the literature analysis on the application of ZnO in SOFCs, we studied the effect of forming pressure (84–336 MPa) on the sintering of zinc oxide ceramics.

According to SEM fractography, the fracture of ZnO ceramics is brittle [24]. As for its micromechanism, the fractographic analysis indicated that all samples obtained at different pressures and a sintering temperature of 1 100 °C show chipping.

Data on the electrical properties of ZnO ceramics after being formed under different pressures and sintered at various temperatures are presented in Arrhenius coordinates in Figure 9. The linear dependencies in wide temperature ranges correspond to the ceramics with zero porosity, and nonlinear curves are referred to the porous samples. Analysis of electrical conductivity data concludes that the ionic conductivity can be adjusted by changing the forming pressure of the powders. Red (sintered at 1 100 °C and pressed at 336 MPa) and green (sintered at 1 200 °C and pressed at 168 MPa) curves clearly indicate the possibility of reducing the sintering temperature when the pressure is doubled to achieve similar ionic conductivity values, which gives the possibility to develop materials with different alloying elements and properties.

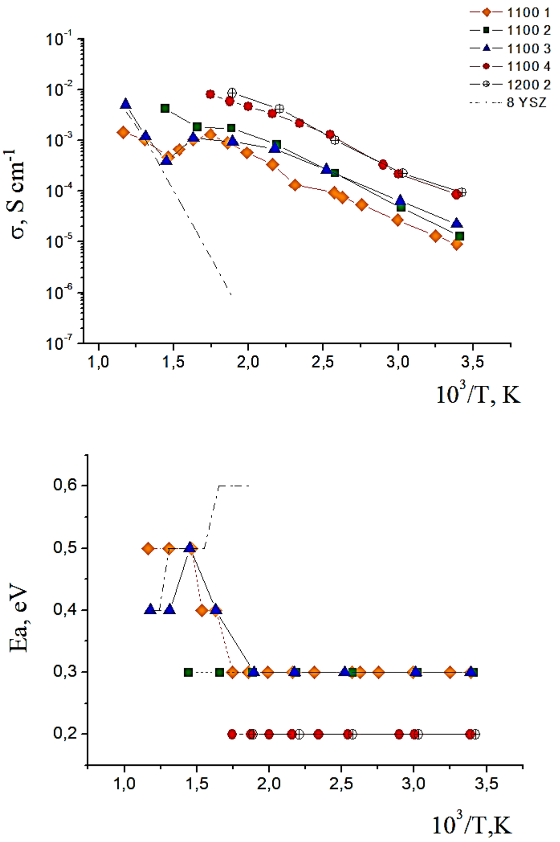

Figure 9 – Electrical conductivity and activation energy of ZnO ceramics pressed at different pressures and sintered in the range of 1 100–1 200 °C: 1 – 84 MPa; 2 – 168 MPa; 3 – 252 MPa; 4 – 336 MPa

Comparing the activation energies of zinc oxide and yttria-stabilized zirconia (marked as 8YSZ, dashed line at Figure 9) materials in the temperature range from room temperature to 600 ºC, the decrease of E_a value with temperature is observed for zinc oxide. Such behavior is attributed to zero porosity of ZnO ceramics (red lines). The activation energy increases by 0.1–0.2 eV with the porosity and depends on the temperature in the range from 300 ºC and above, which should be considered when forming the porous structure of the electrodes. In the case of 8YSZ-based ceramics with only oxygen conductivity, the activation energy increases with decreasing temperature. ZnO electrolyte with a thickness of 75–85 μm and diameter of 13–15 mm after sintering at 1 100–1 200 °C was used for testing in real fuel cell operation conditions without structural optimization membrane-electrode complex. The open-circuit voltage of 1.07 V was obtained at 450 °C.

Platinum-rhodium grid, which has a limited catalytic surface (catalytic layer), was used as electrodes. The current density of 0.36 μA/cm^2 was obtained at a voltage of 0.6 V and a temperature of 500 °C [26, 28]. The obtained results confirm the effectiveness of using the method for materials characterization without structural optimization of membrane-electrode complex and can be used to search for promising fuel cell materials. The sensitivity of the test system is 2.5 pA.

5 Conclusions

It can be concluded that the application of zinc oxide in fuel cells is a promising area of research. However, the complexity of the processes occurring in the electrode-membrane complex requires step-by-step analysis of each element (anode, cathode, and electrolyte), structural and chemical composition optimization, and tests at real FC operation conditions. The small number of studies on using pure zinc oxide as the SOFC electrolyte opens opportunities for thorough analysis and determination of optimal technological parameters that will accelerate the implementation of SOFCs with operating temperatures below 600 °C. As follows from the review of ZnO-based materials for SOFC, the materials with mixed conductivity and low sintering temperatures are the most promising and effective for electrochemical conversion in real FC operation conditions. Moreover, the structure optimization of the membrane-electrode complex and testing in real operation conditions will accelerate the implementation of fuel cell technologies to achieve a zero-carbon target. The method for analysis of promising materials without structural optimization was investigated. The current density of 0.36 μA/cm^2 was obtained for the fuel cell with 75–80 μm thick ZnO electrolyte and without membrane electrode assembly optimization at a voltage of 0.6 V and a temperature of 500 °C.

The paper presents the steps of increasing the catalytic activity of the fuel cell electrodes, which are useful in modeling the profile of the catalytic layer and its subsequent verification in real conditions.

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