Directions for Solving Design and Long-Term Operation Problems of Solid Oxide Fuel Cell Installations

Ramiz Hasanov[1], Riad Naghiyev[2] , Saida Musevi[3]
[1]Azerbaijan State Oil And Industry University
[2]Azerbaijan State Oil And Industry University
[3]Azerbaijan State Oil And Industry University

Abstract

The thermo-mechanical analytical model proposed for different solid oxide fuel cell (SOFC) designs addresses the deformation behavior and mechanical stability of SOFCs at various thermal stresses, specifically the creep resistance and the long-term endurance beyond the elastic limit.

The model considers the deformation of multi-layer SOFC in the temperature range of 600–800°C and presents the combination of the correlated parameters for SOFC performance evaluation, stability and long-term endurance under realistic operating conditions and temperature gradients. The numerical analysis of the thermo-mechanical properties of the SOFC materials is presented in terms of mechanical behavior at failure conditions and the influence of rheological and structural properties on SOFC long-term endurance. The SOFC thermal behavior, creep parameters of the SOFC materials and long-term stability are analyzed in terms of stresses, deformations and displacements.

Keywords: modelling, materials, performances, operating temperature, design of compatibility, porous, plasticity, state of equilibrium, thermal strain stresses.

1.Introduction

Conventional energy sources such as gasoline (diesel), coal and hydro source are the main sources for power generation. However, these conventional energy sources are being depleted, and are also unfriendly to the environment. Alternative energy sources such as renewable energy (RE) systems are becoming more popular in power generation applications. RE sources include solar energy, wind energy, photovoltaic (PV) cell energy, fuel cell etc which are very effective in reducing the green house gas emissions. In the near future, large portions of increase in electrical energy demand will be met through widespread installation of distributed generation (DG). Many advantages are considered for application of DG, i.e., increased service reliability, reduction of the need for grid reinforcement, generation expansion and power factor correction. Furthermore, it is possible to improve voltage regulation and local power quality more precisely using DGs in comparison to conventional centralized generators. DG sources comprise of direct energy conversion sources producing DC voltages or currents such as fuel cells and photovoltaic sources, high-frequency sources such as micro turbines, and variable frequency sources such as wind energy. Power generation from solar energy sources and wind energy sources is unpredictable, because solar power depends on the availability of sun light and wind energy system depends on the wind. Since fuel cells have no geographical limitations, they are preferred for small scale power generation. Power generation in fuel cells depends on the hydrogen input which is available in abundance. Further, fuel cells are known for their low to zero emissions, high efficiency (35-60%) and high reliability because of the absence of moving parts. Fuel cells are static energy conversion devices that partially convert the chemical energy of fuels directly into electrical energy and produces water as its byproduct.

The successful utilization of materials requires that they satisfy a set of properties. These properties can be classified into thermal, optical, mechanical, physical, chemical, and nuclear, and they are intimately connected to the structure of materials. The structure, in its turn, is the result of synthesis and processing. A schematic framework that explains the complex relationships in the field of the mechanical behavior of materials, shown in Figure 1, is Thomas's iterative tetrahedron, which contains four principal elements: mechanical properties, characterization, theory, and processing. Interrelationships among structure, properties, and processing methods, the most important theoretical approaches, and the most-used characterization techniques in materials science today.

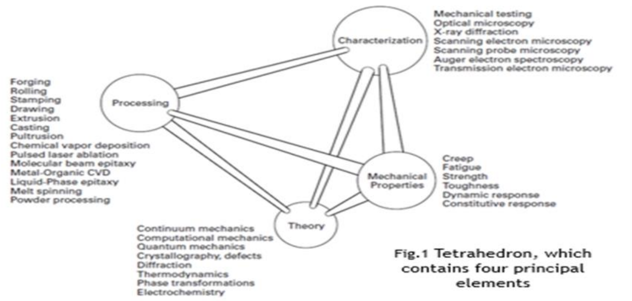


Fig.1 Tetrahedron, which contains four principle elements

Clean and sufficient energy is an important precondition for the continued growth in global wealth. Solutions must be found to utilize the remaining fossil fuels more efficiently and also to ensure that new environmentally friendly fuels can secure power production in the post-fossil fuel era. This is the essence of the global energy challenge. Fuel cells hold the promise of an efficient, low pollution technology for production of electricity. Because fuel cells rely on electrochemical rather than thermo-mechanical processes in the conversion of fuel into electricity, the fuel cell is not limited by the Carnot efficiency as is the case for conventional generators. High-temperature fuel cells hold the

Hasanov Ramiz Aliş oğlu , professor of Azerbaijan State Oil and İndustry University ,+994502572401,Baku S. Vurqun Street 36/30, ramiz.hasanov52@gmail.com

promise of an efficient, low pollution technology for production of electricity and efficient use of waste heat including low transmission losses. Scalability, decentralization, and load following capabilities are major advantages that can play an effective role in future power grids and power supply.

Solid oxide fuel cells offer the potential of high volumetric power density, cost efficiency, and fuel flexibility, and significant progress has been made during the last 5 years in bringing SOFC technology closer to commercialization.

This entry will endeavor to answer the question whether SOFC technology is now ready for the market or perhaps put in another way: Is the market ready for SOFC technology and which challenges still need to be addressed? Requirements to SOFC design: There are six main types of fuel cell: alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), polymer electrolyte membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC), solid oxide fuel cell (SOFC). The entry will describe how SOFC technology can contribute to solving the energy challenges in the future. The current status of the SOFC technology and industry will be briefly discussed and the possible markets described. Three main challenges on the road to competiveness – life- time, reliability, and cost – are addressed. Techno-economic studies of the different market segments are used to define the threshold for market entry. The entry ends by looking ahead and concluding that the SOFC technology is ready for the market with respect to the projected cost and lifetimes, but that reliability under real-life conditions still remains to be demonstrated. The learning investments needed, however, do not appear to be prohibitive considering the benefits which this game - changing technology has to offer. Among different types and scale power generation systems, fuel cells have received more attention, because they can provide also both heat and power. Advantages of SOFC Fuel Cells are:

- Higher electrical efficiency. The SOFC technology will be able to provide an electrical efficiency of up to 60%. This efficiency is very high compared to worldwide power plants operating at average electric efficiencies of 30–35% and to existing decentralized, smaller power generation equipment (engines and generators) operating at as low as 5–10% for engines and 15–25% for generators. Application of SOFC units with higher electrical efficiency will result in substantial savings in fuel and money, and for operation on fossil fuels also in a proportional reduction in CO2 emissions;

- High efficiency for all capacities. The SOFC technology is scalable and can cover the complete range from 1 kW to 1 MW, or even higher, with almost no loss of efficiency. The technology offers a very competitive output per weight or volume compared to power plants. Because of this, the SOFC technology addresses a wide range of applications and finds use both in urban and remote areas and both for stationary and mobile purposes;

- Fuel flexibility. The SOFC technology is (together with MCFC) the only technology among the different fuel cell technologies which is able to effectively generate power directly based on the fossil fuels in use today, and at the same time, the technology has a clear path to renewables and CO2-neutral energy systems. This is due to the higher operating temperatures and the superior ability of the SOFC to convert hydrocarbon in the fuel cell stack. - Lower maintenance cost. The SOFC system provides a highly effective and direct electrochemical conversion of fuel to power. The only rotating parts in the system are a fuel pump and a small air blower. Accordingly, maintenance costs are expected to be substantially lower, and operating periods between overhauls are substantially longer than conventional technologies.

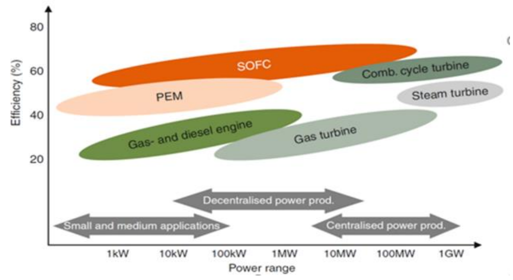


Fig. 2. SOFC compared with other power production technologies (illustrative figures)

2. Experimental

Materials and Methods:

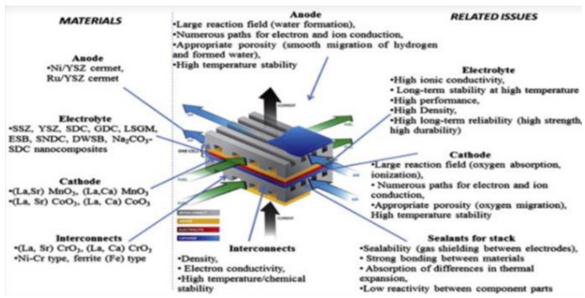


Fig. 3. Characterization of SOFC material support. (Yokokawa,H. 2003)

Structural strength of materials – a set of mechanical properties that ensure reliable and long-term operation of the material under operating conditions depend on a number of factors (fig.4)

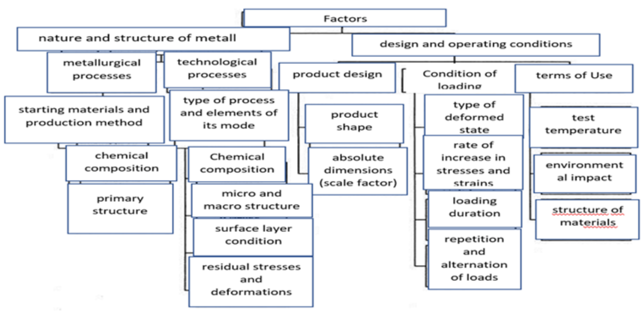


Fig 4. Factors define reliable and long-term operation of the material

According to the work is planned to study ma-terials of different structural content exposed to operating temperature during the operation of the facility, namely (Figure 5):

1. Dense structure, based on zirconium (Zr); 2. Porous structure, based on titanium (TI); 3. Materials based on transition metals, so-called Max Phase in different chemical composition.

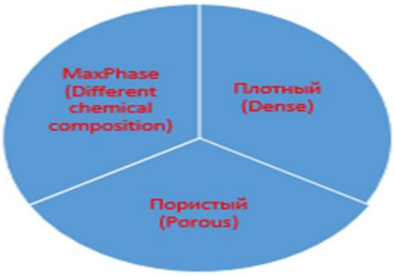


Fig.5. Used Material structure type

Creation of materials with given and desired properties to ensure a higher consumer quality of devices by synthesizing compatible combinations of the indicated disciplining factors and structural properties of materials [7, 8]

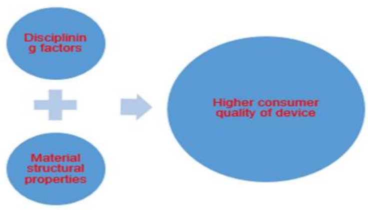
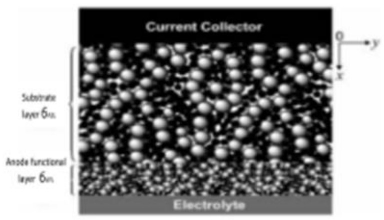


Figure 6. Creation of materials with given and desired properties

The structural properties of the materials used for SOFC elements (mainly their porosity) significantly affect their operational performance and are associated with their deformation behavior, which is accompanied by structural variability. These processes are also associated with the structural variants of the elements and the device in general. Thus, the study of the structural changes associated with the material supply of its elements (Fig. 7, 8) is an area of research that attracts attention, in which the operational processes of the structural operation of the device built on various elements are noted.



Fiq. 7. Schematic view of a two layer porous composite anode (Zenga, S., 2017)

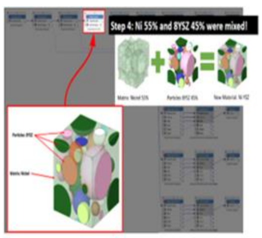


Fig.8. Sample of obtaining the porous structure

Structural elements of operating process equipment in a deformable state especially for long-term operation that exist under high operating performances and in the course of activity are exposed to strong deformations. In the past, of these elements deformations, material of which characterized by a nonlinear character have been extensively investigated (Antman S.(2005) - Vasilev A.,1989). Importantly, these studies of various deformation processes in element's material allowed to predict the corresponding impacts of the deformation processes to the operating efficiency. In this regard, the numeric study of inelastic deformations under different conditions in porous structural elements during different stages of their exploitation and under non-equiaxial loading (Hasanov, 2011) has been performed. Furthermore, (Holm B., 2010) new experimental data has been generated on the strain hardening behavior in samples under operating conditions.

2.1 Influence of the elements surface

Influence of the elements surface on the stability of the SOFC design:

The third direction of work – to study of porous materials for use in the practice of designing a device as a whole and their elements. This issue has been discussed many times with project partners. With his great support and faith in the possibility of application in the practice of creating devices, the following task has been set and solved:

Development goal – the study of the deformation behavior of porous structure and the determination of an adequate deformation model for this behavior, taking into account mass transfer processes in a dynamic model for planning and effective implementation of various measures aimed at designing devices using of a similar material structure.

Task content:

1. The problem of determining a mathematical model of deformation behavior and studying, on this basis, the stress-strain state of porous structure under quasi-static and dynamic loading is being solved.
2. The presence of mass transfer during loading, etc. the dynamism of porous structure distinguishes and is decisive for choosing their equations of state.

Problem solution:

The mathematical model of deformation behavior for studying the stress-strain state of any medium with a porous structure includes 21 equations, of which:
- 9 equations of the form $\varepsilon = \varepsilon(u)$ define geometric ratios;
- 9 equations of the form $\sigma = \sigma(\varepsilon)$ define physical ratios;
- 3 equilibrium equations (or equations of motion if dynamic loading is considered).

Source dependencies:
1. A porous structure is considered, inclu ding a solid phase from the skeleton of the structure and a phase of the filling pore.
2. Reduced modulus of elasticity porous structure is defined as [1]

$$E_{pr} \frac{m_s E_s + m_g E_g}{m} \qquad (1)$$

, where Epr is the reduced modulus of elasticity; m, ms, mg are, respectively the Young's modulus of the skeleton and the medium that fills the pores under compression. During operation, the porous structure is also deformed under the influence of external factors. This contributes to the migration of the medium filling the pores in the direction of the pressure gradient - P in the pores, as a result of which the volume of the medium filling the pores changes, i.e. as a view from (1) E_{pr} is a function of time and therefore:

$$E'_{pr} = \frac{m_s(E_g - E_s)}{(m_s - m_g)}\, m'_g \qquad (2)$$

Under quasi-static loading, which provokes a slow change in the stress state of the porous structure due to displacement, the mass of the medium filling the pores mg decreases (how many this is also question and must be defined!! This task is currently being studied)

Dependency analysis for Epr:

1. It is assumed that only mg changes with time, i.e. mg < 0;
2. For most porous structures Eg < Es;
3. Then from (2) due to the fact that ms(Eg − Es) < 0 and mg < 0, then $E_{pr} > 0$, which means that over time the reduced modulus of elasticity for a porous structure, containing a certain medium in the pores increases, i.e. the tension diagram between the normal stress "σ" and the relative strain ε for uniaxial tension in various modes (see Figure 9) will have the form (see Figure 10).

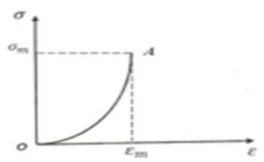


Figure 9. Tension diagram of a porous and non-porous structure, the pores of are filled with a medium, where σ_m, ε_m are the maximum values, respectively, of stress and strain.

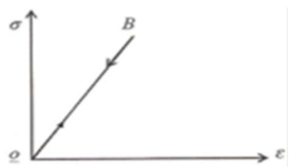


Figure 10. Tension diagram of a porous structure, the pores of which are filled with a medium (high-speed loading).

Thus, we can conclude that when the stress-strain state of a porous structure is studied, depending on the loading rate, different equations of state should be used, i.e.:

1. With dynamic processes, i.e. under impulse loads, the dependence σ = σ(ε) is represented by a straight curve, as a result of which the equation of state can be expressed by the Hook law.

2. Under quasi-static loading, i.e. for time-distributed loads, the application of the HUK law can lead to large inaccuracies (up to 80%). This is especially true for porous structures, in which the loading process is characterized by the presence of mass transfer and which have deformation characteristics that coincide with the characteristics for elastic-nonlinear bodies.

Thus, the equation σ = f(ε) of the load diagram branches can describe both plastic and nonlinear elastic deformation of a body with a porous structure.

Hence, to obtain the equation of state for porous body, the equation of state for structures with an elastic-plastic characteristic can be used.

Consequently, as a result of the analysis of the dependence that determines the change in one of the mechanical indicators - the reduced modulus of elasticity for the porous structure, two possible variants of its loading, different in terms of deformation behavior, have been established, namely:

1. Quasi-static (the reduced modulus of elasticity Epr increases);
2. Speed loading (the reduced modulus of elasticity Epr remains permanent).

As the initial equation, the functional dependence for elastic media in the form of the stress tensor σij on the components of the strain tensor εij , the components of the metric tensor gij and external disturbances (temperature, pressure and radiation dose) in various combinations is used, which is represented by the dependence below:

$$\sigma_{ij} = f_{ij}(\varepsilon_{\alpha\beta}, g_{\alpha\beta}, T - P, D), \quad i,j,\alpha,\beta = 1,2,3 \qquad (3)$$

To determine the equation of state for elastic and elastic-plastic structures in a general form, the method of expansion in a Taylor series of the original above equation was used to study the functional dependence σij and εij at T, P = constants, D = 0, which is presented both for stresses and for deformations:

$$\sigma_{ij} = Pg_{ij} + Q\varepsilon_{ij} + R\varepsilon_{ik}\varepsilon_{kj}, \quad i,j = 1,2,3$$
$$\varepsilon_{ij} = Ag_{ij} + B\sigma_{ij} + C\sigma_{ik}\sigma_{kj} \qquad (4)$$

where P, Q, R are functions of the invariants of the strain tensor and the stress tensor . In a particular case, it is assumed that P = lq, Q = 2m, R = 0, l, m – Lame coefficients; q = eij gij – relative volume change or the first strain invariant

To describe the deformation behavior of elastic-plastic structure, an analogy was used between the deformation characteristics of elastic and plastic structures in the processes of loading and unloading, which is based on the assumption that there are no constant values of the elastic modulus and yield strength for deformable porous structures.

After carrying out a number of mathematical calculations, the equations of state of porous structures were obtained for the variants of their loading, respectively, by quasi static and dynamic loads:

$$\varepsilon_{ij} = (1 - k_0)\left(\frac{1+\nu}{E_s}\sigma_{ij} - \frac{\nu I_1}{E_s} g_{ij}\right)$$
$$\varepsilon_{ij} = \frac{1+\nu}{E_r}\sigma_{ij} - \frac{3\nu}{E_r}\sigma_{ij}$$

Influence of the elements surface on the stability of the SOFC design:

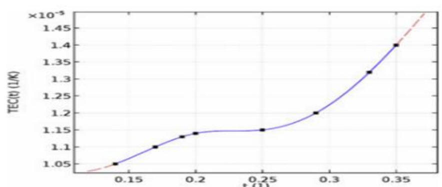


Figure 18. The relationship between porosity and TEC

Table 1

Layer	Young's Modulus[GPa]	Poisson's ratio	Coefficient ther mal ex Pantion (CTE) [10^{-6} K^{-1}]
Anod	220	0.3	12.5
Cathod	160	0.3	11.4
Electrolyte	205	0.3	10.3
Interconnect	205	0.28	12.3

In all models the most commonly used materials were studied to analyze the distribution of thermal stress. The mechanic properties of materials were listed in Table 1 taken from Refs. [8,23]. It should be noted that the material was assumed as linear elastic and isotropic. Fig. 18 showed the anode's coefficient of thermal expansion, which was a function of its porosity. Moreover, the Young's modulus (GPa) and shear modulus (GPa) was a function of porosity, which was the main point all of investigations and could be calculated from the used for that experimentally obtained equations.
The thermal strain stress was enhanced when the temperature increased, which resulted in a thermal expansion, which was different for each material (see table 1). The thermal stress was proportional to the coefficient of thermal expansion (a) and the difference of the temperature distribution (T) and the reference temperature (Tref). The reference temperature was the sintered temperature for the cell's materials and it was set as 800°C, i.e., the thermal strain stress only emerged when the temperature was higher than 800°C.

3. Results and Discussion

Basing on the received results it is possible to draw following results:

1. The relaxation time of the porosity of a porous medium in individual dimensional ratios has a different effect on its deformation behavior.

2. The most appreciable influence renders relaxation time on character of change of the porous body layers porosity. In bodies with it nonlinear elastic the deformable behavior porosity decreases more slowly than in mediums with pronounced relaxation character, and with increase in time of a relaxation rate of decrease in porosity is slows down.

3. In media with a high initial operating pressure, porosity can decrease in layers both in the nonlinear-elastically deformable mode and during relaxation and occurs faster than in media with a low initial pressure of the medium.

4. The pressure in the porous medium and their saturation with environmental products contribute to the relaxation process decreasing faster than in media with nonlinear elastic deformation behavior, and with increasing relaxation time the rate of their decrease intensifies.

5. At the initial stage of operation of a body made of a porous material, a decrease in pressure and saturation with environmental products with a nonlinear-elastic deformable characteristic and with relaxation occurs under the same law, and subsequently, as the object is used, starting from a certain point in time in bodies with a nonlinear-elastic deformable medium and with relaxation there is a slower decrease in pressure and saturation than in bodies with a relaxation environment.

6. As the value of the initial pressure increases, the difference between the corresponding values of pressure and saturation in the case of a medium with relaxation and nonlinear elastic deformation behavior becomes more noticeable: an increase in the initial pressure increases the influence of relaxation processes on the determined values of body pressure and saturation.

7. To maintain stability the deformation behavior of a porous medium in bodies with a relaxation performances is greater than in media with a nonlinear elastic deformable characteristic, and the difference between their values is more significant in the case of media with a high initial saturation pressure.

8. It was found that increasing the operating (pressure) and design (decreasing the porosity and the tortuosity) conditions of the porous layers increase the cell performance.

The calculation results show that, taking into account relaxation processes in porous bodies, its highest values are observed in bodies with a high operating parameters. In other words, it is necessary to take into account the main parameters of the deformation behavior of porous bodies at high operating parameters, which confirms the high effect of relaxation of bodies.

Problems and requirements to fuel elements' production:

1.Two problems are of primary importance in the development of fuel cells, namely a. mechanical and materials science and b. electrochemical. Moreover, the main ones are studies in the field of "a" – MM.

2.It is necessary not to predict mechanical behavior during long-term operation, but to maintain such mechanical behavior that would support the duration of operation;

3.It is necessary not to develop analytical models of deformation and fractal behavior, but to study the deformation behavior of models of solid layered composite bodies with different creep cores and the structure of execution of similar SOFC elements and SOFC as a whole, taking into account the impact of factors in the processes of their production and operation and the oppressive factors accompanying these processes. This means that it is necessary to synthesize materials with structures that have the required creep core, i.e. to study the change in the creep core model during operation under the influence of operating temperatures. Namely, to study the kinetics of the change in the creep core (creep core) during operation (solve the inverse problem to achieve the required service life);

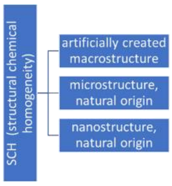
4.Ionic conductivity is good when the thickness is small and the temperature is low. Both of these factors limit the mechanical properties; A stable structure is:
a. High temperature – there is low porosity;
b. Low strength – there is high porosity.

v. The higher the temperature, the lower the porosity
d. The lower the porosity, the lower the strength
e. The higher the porosity, the higher the polarization.

5.To assess the influence of various factors on the deformation behavior of SOFC studies beyond the elastic limit of loading under the influence of operating temperatures, taking into account the design (porous substrate) and structural (pressure in pores) factors;

6.There is no need to predict the service life of the SOFC, but it is necessary to set the service life and solve the problem of reserving the design of the elements and the SOFC itself and increasing reliability;

7.There are two structural levels: Microstructure (grains and boundaries) and Macrostructure (SOFC elements themselves). Each macrostructure, presented as a laminated composite design, has structural and chemical homogeneity (SCH):



4. Conclusions

1. An algorithm has been developed for the synthesis of dense structure materials based on zirconium with properties that are compatible combinations with the operating temperature, shape and metric characteristics of devices from these materials;
2. It has been proven that porous structures are characterized by nonlinear elastic behavior under quasi-static loadings developing in time;
3. The equations of state are obtained and a mathematical model of the deformation behavior of porous structures is formulated to study their stress-strain state, taking into account the corresponding loading modes
4. It has been established that when Hooke's law is used as an equation of state to describe the deformation behavior of porous structures under quasi-static, i.e. loads distributed in time can contribute to 80% distortion of their stress-strain state.
5. The expansion in Taylor series of the original functional dependence was used, which determines the physical and geometric relationships in deformation behavior and, as a result, equations of state were obtained in general form for structure with elastic, elastic-plastic and nonlinear-elastic deformation character rustics.
6. The obtained dependences allow us to investigate various problems of studying the stress-strain state of porous structures under various loadings, determined taking into account implemented technological measures in the process of generating electricity by fuel cells on an anode substrate.

Acknowledgement

The author expresses your own sincere gratitued for this work, which was carried out with the financial support of the project G5949(Lightweight 600ºC solid oxide fuel cells for energy security (LW-SOFC) of the NATO Science for peace and Security Division during the period 2022-2025 years.

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