Development of solid oxide fuel cells using high-frequency plasma spraying technologies

A Platenkin*, V Chernyshov, T Chernyshova and M Dutov

Department of Materials and Technologies, Tambov State Technical University, 106 Sovetskaya Street, Tambov 392000, Russian Federation

*E-mail: lepilalex@gmail.com

Abstract. The paper describes the topical issues and the latest achievements in the development of materials with high electrochemical characteristics for single cells and small assemblies of solid oxide fuel cells (SOFC). The authors propose planar SOFC technology which includes sequential deposition of all layers of a thin-film cell on a porous metallic substrate by plasma techniques. The method allows developing porous SOFC anode and cathode, which increases the active area of electrochemical reaction, reduces the spread of technological parameters (in particular, the spread in thickness and porosity of a solid electrolyte), improves SOFC performance and reduces the mass and size of SOFC assemblies. The paper also describes the physics of plasma spraying process in individual cells and SOFC structures. The proposed method is an alternative to traditional SOFC production methods; it eliminates the necessity to use agglomeration technology or other heat treatment. Moreover, it opens up the prospects for automated continuous production process. The appropriate SOFC production equipment is developed, for stationary and mobile use. Further studies will be focused on the task of reducing the weight of SOFC assemblies, which allows using them as an auxiliary power unit for on-board power supply, for example, for cars, airplanes and spaceships.

1. Introduction

The relevant tasks of all studies currently being conducted in the field of SOFC development include increasing the service life, specific capacity, reducing overall dimensions and, first of all, production costs [1]. The modular principle of SOFC development involves the production of a large number of single cells assembled into a single assembly, along with the stationary SOFC used as combined heat-and-power supply facilities in various industries. SOFC assemblies with minimum size and weight with a power range up to 5 kW are actively used in mobile applications, for example, to secure the on-board power supply for vehicles, airplanes and spacecraft. Such assemblies used as auxiliary power units can function autonomously from the main engine to satisfy the increasing demand for electric energy. It gives a comfort through auxiliary air conditioning and radio communication, and helps to save fuel [2]. However, such application requires SOFC structures with minimum weight and size but high specific capacity.

Informational analysis shows that plasma spraying technology as an alternative to traditional sintering has already been used. For example, in the production of connection contacts in SOFC cathode tubes (Siemens) [3], functional SOFC flat layers (SulzerHexis company) [4], tubular SOFC (Mitsubishi company) [5]. This technology has also been used for protective coatings of SOFC joint plates [6]. Relying on the latest achievements in the sphere of plasma techniques the authors propose new plasma spraying technology with a modified plasmatron - inductor that induces plasma jet by a high-frequency (HF) magnetic field [7]. The paper also introduces the methodology for producing planar SOFC with
the sequential deposition of all layers of a thin-film cell on a porous metallic substrate. The proposed method allows using direct current plasma induced by a high-frequency field for the synthesis of SOFC materials and for deposition of cathode layers of Perovskite-type oxides.

2. Plasma spraying technologies for SOFC fabrication

Standard SOFC production technologies are based on the traditional methods of processing and sintering of wet ceramic powder, for example, sintering in castings, screen printing or spraying wet powder [8]. Such techniques are effective ways to improve product quality and to reduce energy and material costs. As an alternative approach to small-size SOFC development the authors propose a modified thermal plasma deposition technology based on direct current plasma induced by high frequency radiation. The figure 1 shows a standard direct-current plasmatron with Laval nozzles (figure 1a) and a plasmatron with an additional inductor to create a high-frequency magnetic field that influences plasma jet (figure 1b).

Figure 1. Direct-current plasmatron with Laval nozzles (a), modified plasmatron with an inductor to create a high-frequency magnetic field around the plasma jet (b).

DC plasma generation is based on the interaction of a gas, in our case argon, with a high-current arc discharge between the finger-shaped cathode and the hollow anode that forms a fast and very hot plasma jet (T > 10⁴ K). Laval nozzles provide the controlled expansion of a plasma jet and accelerate the jet to supersonic speeds of 2000-3000 m/s. Sprayed powders are introduced radially into the plasma, where they are accelerated, melted, and finally projected onto the substrate. The coating is formed in the process of solidification and flattening of particles on the substrate. High-speed nozzles allow achieving the increased rates of atomization of particles into a plasma jet, up to 900 m/s, which is approximately two times higher than with standard nozzles [9].

To generate HF-induced plasma the standard plasmatron is equipped with an inductor that exposes plasma jet to high frequency radiation. The powder is introduced axially into the hot plasma core (T> 10⁵ K). Compared to direct-current plasma, HF plasma jet has a larger volume, but lower speed, guaranteeing a long and intense interaction of raw materials and plasma in a long jet. This technology makes it possible to increase the rate of plasma-chemical synthesis and the simultaneous deposition of
SOFC obtained from liquid and powder raw materials. Liquid and powder anode, solid oxide and cathode materials are fed into the plasmatron through a peristaltic pump and are sprayed through a spray probe [10]. The proposed construction allows controlling both the rate of plasma-chemical reactions and the deposition rate of SOFC layers, so as to obtain the required physicochemical parameters of all the elements of SOFC construction.

3. Methodology (plasma-chemical sputtering model and SOFC fabrication)

The first generation of SOFC had a structure based on a solid electrolyte with a thickness of 150-200 mcm. It served as a basis for other components (anode, cathode, etc.). Since ohmic losses are mainly caused by the thickness of electrolyte, the study was focused on reducing the thickness of electrolyte, and the modified SOFC construction is based on electrodes (basically anodes) or special substrates on which all other layers of SOFC construction are applied.

Figure 2 shows a planar thin-film structure on a metallic substrate fabricated using the proposed plasma spraying technology.

![Figure 2](image)

Figure 2. Model of planar SOFC fabricated by plasma spraying.

The transition from ceramic to metallic porous substrate reduces the problem of cracking, reduces the weight and size and simplifies SOFC construction which leads to large cell sizes and simplifies battery construction.

The porous metallic substrate provides SOFC mechanical strength and has an excellent electrical and thermal conductivity, which improves SOFC performance, and the high porosity of the substrate ensures even distribution of fuel gas over the entire area of construction. Controlled HF-induced plasma deposition allows simultaneous deposition of anode, electrolyte and cathode layers on a substrate, which provides a small technological spread of parameters and secures homogenous structure. Controlled HF-induced plasma deposition allows simultaneous deposition of anode, electrolyte and cathode layers on a substrate, which provides a small technological spread of parameters and secures homogenous structure.

Such construction with a porous metallic substrate requires the use of a long-term stable and corrosion-resistant material with adequate thermal expansion behavior, associated with ceramic cell components. Fabrication of such metallic substrate is an important trend in the development of plasma chemical spraying technology.

After analyzing plasma spraying experiments the authors proposed two stack constructions, for stationary and mobile use, with ferrite steel joints. Figure 3a shows stack construction for stationary use with a relatively thick machined connecting plate, frame and cell assembly.
4. Experiments to verify the proposed method

The main element of the cell, membrane-electrode assembly (MEA), should have a high porosity (> 20%) of electrode layers, but, on the other hand, a very low closed porosity of electrolyte (less than 2%). Porous substrate (e.g. Ni felt) ensures even distribution of fuel gas over the entire surface area and guarantees the initial porosity (> 20%) of electrode applied to the substrate. Electrolyte porosity level < 2% is achieved by adjusting the rate of HF-induced plasma sputtering.

To achieve the optimum qualities of MEA layers experiments concerning the materials and processing parameters were carried out. Table 1 provides the data on powder raw materials used for the MEA production.

Table 1. Powders used for the production of cells by plasma spraying.

| Powder                  | NiO | ZrO$_2$-7 mol%Y$_2$O$_3$ | ZrO$_2$-10 mol%Sc$_2$O$_3$ | (La$_{0.8}$Sr$_{0.2}$)$_{0.98}$MnO$_3$ |
|-------------------------|-----|--------------------------|-----------------------------|---------------------------------------|
| Short name              | NiO | YSZ                      | ScSZ                        | LSM                                   |
| Morphology              | sintered, ground | sintered, ground | sintered, ground | sintered, ground |
| Size distribution       | 10-25 µm | 5-25 µm | 2-20 µm | 20-40 µm |

Applied metallic substrates are nickel felt or ferrite steel constructions with porosity in the range of 50-80%. Nickel manifests excellent oxidation-resistant properties but has a high thermal expansion mismatch with the ceramic cell components, which causes serious problems when substrates are large enough. Ferrite steel has a higher coefficient of thermal expansion, but its corrosion resistance is lower. High-speed plasma technology is used for apply dense high-melting electrolyte coatings made of yttrium-stabilized zirconium (YSZ) with a thickness of only 20-40 µm. Figure 4 shows metallographic cross section of a planar cell obtained by plasma spraying on a direct-current plasmatron without a HF field. It consists of a porous metal-ceramic NiO/YSZ anode with a thickness of 35 µm, 25 µm thick dense electrolyte and a porous 30 µm thick cathode deposited on a porous nickel-felt substrate.

![Figure 3. SOFC battery for a) stationary and b) mobile use (as a secondary power source).](image)

![Figure 4. Metallographic cross section of a cell obtained by plasma spraying on a nickel-felt substrate.](image)
Quantitative analysis of images shows the residual porosity of electrolyte layer in the range of 1-2% with closed pores. After the reduction of NiO to Ni a further increase in anode porosity occurs, as a result, the porosity reaches a sufficiently high level in the range of 20-25%. Cathode, however, is not affected by “pore formation process”, which leads to limited porosity of only 10-15%. Impedance spectroscopy shows that the relatively low porosity influences considerably polarization resistance of a cathode cell. Therefore, additional efforts are required to improve the structure of the cathode pores. A promising approach to this problem is the development of porous cathode coatings from liquid precursors using HF plasma technology, which this paper did not consider. Electrochemical analysis of small round cells with a size of up to 15 cm² obtained on a nickel-felt substrate identified high specific power of up to 800 mW·cm⁻² under operating voltage and temperature of 0.7 V and 900 °C. H₂ and air served as operating mediums, stabilized zirconium (ScSZ) was used as an electrolyte. At lower operating temperatures, specific power decreases with temperature. As it shown in the figure 5, specific power is still quite high (400 mW·cm⁻²) at a working temperature of 800 °C.

Figure 5. Current-voltage characteristic of a cell (15 cm²) obtained by plasma spraying on a nickel-felt substrate, with H₂ and air as operating mediums, at different working temperatures.

During the scaling process, the cells with a size of 100 cm² (10x10 cm²), containing YSZ electrolyte, were fabricated. The supporting substrate influences considerably electrochemical characteristics, providing high porosity of electrodes Figure 6 shows current-voltage characteristics of two cells of 10 × 10 cm² in size (85 cm² active area), which contain various substrates, nickel felt and ferrite foam, correspondingly. The remaining 15 cm² of substrate area are allocated for pads and fasteners.

Open-circuit voltage of a cell containing Ni-felt is significantly lower compared to a cell with a FeCrAIY substrate. This may be caused by a higher thermal expansion of Ni, which contributes to the appearance of micro-cracks in the thin plasma sprayed electrolyte YSZ. However, a cell supporting the Ni layer acquires a higher specific power of approx. 400 mW·cm⁻² at 0.7 V and 900 °C (H₂/air), which is explained by a higher oxidation resistance and, probably, by a higher electrochemical activity of Ni substrate compared to FeCrAIY substrate, where the specific cell power is only 200 mW·cm⁻². Impedance spectroscopy showed an uneven distribution of gas within larger cells, which may cause diffusion polarization resistances.
Figure 6. CVC of cells obtained by plasma spraying (active area of 85 cm²) containing various substrates (Ni felt, foamed FeCrAlY) at 900 °C.

At a reduced operating temperature of 800°C specific power slightly decreased up to 180 mW·cm⁻² at 0.7 V and 225 mW·cm⁻² maximum. Further improvement of electrochemical characteristics can be achieved through an improved sealing technology and through the use of new optimized materials and substrate structures which are currently under development.

Conclusion
A new method for manufacturing SOFC cells and stacks for stationary and mobile devices is developed. The method is based on the processes of plasma deposition on a porous metallic substrate, which makes it possible to obtain highly porous SOFC anode and cathode layers so as to increase reducing reaction area and to reduce weight and size while maintaining specific power requirements.

The standard plasmatron is modified by adding an inductor which generates high-frequency magnetic field around the plasma jet. This technology makes it possible to control the process of SOFC layers deposition and to obtain layers with higher electrochemical characteristics.

It is shown that the content and structure of supporting substrates and the appropriate sealing technology largely determine the electrochemical parameters of larger cells. The technology to fabricate stationary and mobile SOFC stacks is proposed. Further studies should involve the development of new types of substrates. A series of electrochemical studies and experiments were conducted, including fast heating and thermal cycling experiments that justified the high efficiency of the proposed methodology, especially in the sphere of producing mobile equipment, such as auxiliary power units.

References
[1] Sanghoon J, Gu Y, Wonjong Y, Pei-Chen S, Min H and Suk W 2015 Plasma-enhanced atomic layer deposition of nanoscale yttria-stabilized zirconia electrolyte for solid oxide fuel cells with porous substrate. ACS Appl. Mater. Inter. 7(5) 2998 https://doi.org/10.1021/am508710s
[2] Kobayashi K and Sakka Y 2014 Research progress in nondoped lanthanoid silicate oxyapatites as new oxygen-ion conductors. J. Ceram. Soc. Jpn. 122 921 https://doi.org/10.2109/jcersj2.122.921
[3] Jaffar S 2002 Conductivity of yittria-stabilized zirconia nanostructure electrolyte for solid oxide fuel cell application by using rf magnetron sputtering. Adv. Mater. Res-Switz. 268 352 https://doi.org/10.4028/www.scientific.net/SSP.268
[4] Muller M, Bouyer E, Bradke M, Branston D, Heimann R, Henne R, Lins G and Schiller G 2002 Thermal induction plasma processes for the synthesis of sofc materials. Adv. Mater. Res-Switz.
[5] Haart J, Vinke I, Janke A, Ringel H and Tietz F 2001 New developments in stack technology for anode substrate based sofc. ECS Proceedings Volumes 16 111 https://doi.org/10.1149/200116.0111PV

[6] Lee S, Lee Y, Parka J, Yu W, Cho Y, Kima Y and Cha S 2019 Effect of plasma-enhanced atomic layer deposited YSZ inter-layer on cathode interface of GDC electrolyte in thin film solid oxide fuel cells. Renew. Energ. 144 123 https://doi.org/10.1016/j.renene.2018.11.021

[7] Cheng F and Sun J 2019 Fabrication of a double-layered Co-Mn-O spinel coating on stainless steel via the double glow plasma alloying process and preoxidation treatment as SOFC interconnect. Int. J. Hydrogen Energ. 44 33 https://doi.org/10.1016/j.ijhydene.2019.05.060

[8] Platenkin A, Chernyshov V and Chernyshova T 2019 Concentration of nano-sized objects in plasma-chemical material: Estimation by tunnel resonance method. J. Phys. Conf. Ser. 1145 012014 DOI: 10.1088/1742-6596/1145/1/012014

[9] Liu J, Wang S and Hsu Y 2018 Solid oxide fuel cells with apatite-type lanthanum silicate-based electrolyte films deposited by radio frequency magnetron sputtering. J. Power Sources 381 101 https://doi.org/10.1016/j.jpowsour.2018.02.007

[10] Fondard J, Bertrand P, Billard A, Fourcade S, Batocchi B, Mauvy M, Bertrand G and Briois B 2017 Manufacturing and testing of a metal supported Ni-YSZ/YSZ/La2NiO4 IT-SOFC synthesized by physical surface deposition processes. Solid State Ionics 310 10 https://doi.org/10.1016/j.ssi.2017.07.027