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Protective-conducting coatings based on black glasses (SiOC) for application in Solid Oxide Fuel Cells

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ABSTRACT

The main aim of the presented study was to investigate the possibility of application of one of the newest group of materials – black glasses, in the form of protective-conducting coatings on metallic interconnects in Solid Oxide Fuel Cells (SOFC). Materials, obtained using the sol-gel method, with use of novel silsesquioxanes precursors, were deposited on ferritic stainless steel Crofer 22APU substrate via dip-coating and then heat-treated in protective atmosphere of argon at 800 °C. Structural studies of the resulting coatings i.e. XRD and MIR confirm formation of black glass structure while microstructural studies i.e SEM with EDS allowed to assess their compactness and homogeneity. The effectiveness of black glass coatings in the protective role was evaluated by the oxidation kinetics tests performed for 100 h in a laboratory air atmosphere at 800 °C in isothermal conditions. Additional microstructural studies (SEM with EDS and XRD) of both surfaces and cross-sections of the tested samples, after treatment in the simulated aggressive working environment of SOFC, proved protective properties of the investigated materials. The electrical properties of coatings were studied with the use of direct current (DC) two-probe four-point technique at temperatures ranging from 500 to 800 °C, showing an acceptable level of the area-specific resistance of the oxidized coatings around 0.1 [$\Omega \cdot cm^2$]. The presented results show that the black glass-based protective-conductive coatings have a significant potential in the proposed application.

Introduction

In the era of environmental problems caused by humans such as global warming and greenhouse effects, one of the biggest challenges is an increasing demand for energy. As far as the environmental protection and the increasing amounts of fossil fuels consumption are concerned, the concept of the so called "indirect" technologies i.e. Solid Oxide Fuel Cells seems to be a very promising solution in comparison with conventional technologies. Not only is the level of greenhouse gases emission significantly decreased, but also fuels supplying traditional devices can be used. Additionally, they exhibit simplicity of construction, minimum air pollution and high efficiency of the whole system [1,2]. Low power output and voltage of a singular SOFC with YSZ (Yttrium Stabilized

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Zirconia) electrolyte cause that SOFCs for real applications have to consist of multiple cells grouped into stacks – bigger units in which the power output and current densities are sufficiently multiplied. It is accomplished by the use of interconnects in the form of bipolar flat panels equipped with channels, which allow undisturbed flow of reagents and reaction products during cell's operation [1]. As a crucial part of the system, apart from providing mechanical stiffness as a constructive element, interconnects play other important roles such as [2]:

a) gas separation of anodic and cathodic reaction spaces,
b) providing an electrical connection between cells in stack,
c) direct transfer of electric current to the external receivers.

Interconnects work under very harsh conditions including high temperature (600 °C÷1000 °C) and an aggressive, oxidizing-reductive atmosphere resulting from the difference in oxygen partial pressures between anodic and cathodic spaces (additionally high gradient of oxygen chemical potential occurs) [3]. Only a few materials can fulfill such rigorous requirements. Ferritic stainless steels are one of the most promising materials group for application as interconnects in SOFCs [4,5]. Numerous such steels e.g. E-brite, Crofer 22APU, AISI 441 or Sandvik Sanergy HT were developed in order to meet these specific requirements and work efficiently under extreme conditions [6–8]. Unfortunately, during their exploitation harmful gaseous Cr compounds are created, which may pollute electrodes' spaces. Also, protective Cr_2O_3 scale formation on the ferritic stainless steel substrates is often too fast, which may cause deterioration in electric properties of interconnect element. In order to protect the material from the destructive influence of working conditions, protective-conducting coatings are used. Such coatings should provide the material with appropriate electric properties and satisfactory corrosion protection [1,2,9].

Black glasses are a recently developed group of materials, whose properties can be easily tailored by altering the synthesis parameters. They are based on Silicon Oxycarbide SiOC with structure of amorphous silica, in which carbon C^{4-} anions replace a part of O^{2-} ones. The main aim of such replacement is the local increase in the bond density in the structure, in order to strengthen the network of chemical bonds within the structure. This results in excellent thermal, chemical and mechanical properties as well as high resistance to oxidation [10–12].

However, the black glass structure can incorporate only a limited amount of carbon. If a certain threshold is exceeded, the excess carbon appears as “free carbon” phase. Its presence is responsible for black color of glasses and leads to interesting electrical properties of the material [13,14]. In the literature, there can be found two main theories concerning structure of black glasses with the content of free carbon, depending on temperature range in which material is obtained. According to [13–15], up to 800 °C, free carbon appears in the form nanodomains of graphite dispersed in the glassy matrix (Fig. 1-I), while in higher temperatures over 1000 °C, amorphous SiO_2 is enclosed in a graphene network (Fig. 1-II).

Properties of black glasses can be adjusted in a very broad range by changing the amount of carbon ions incorporated into the silica glass network. As a result, via appropriate choice of precursors, materials with desired properties, from the point of view of their possible applications, can be obtained. Besides, lack of shrinkage and sintering resistance allow to use them in the form of coatings [16,17].

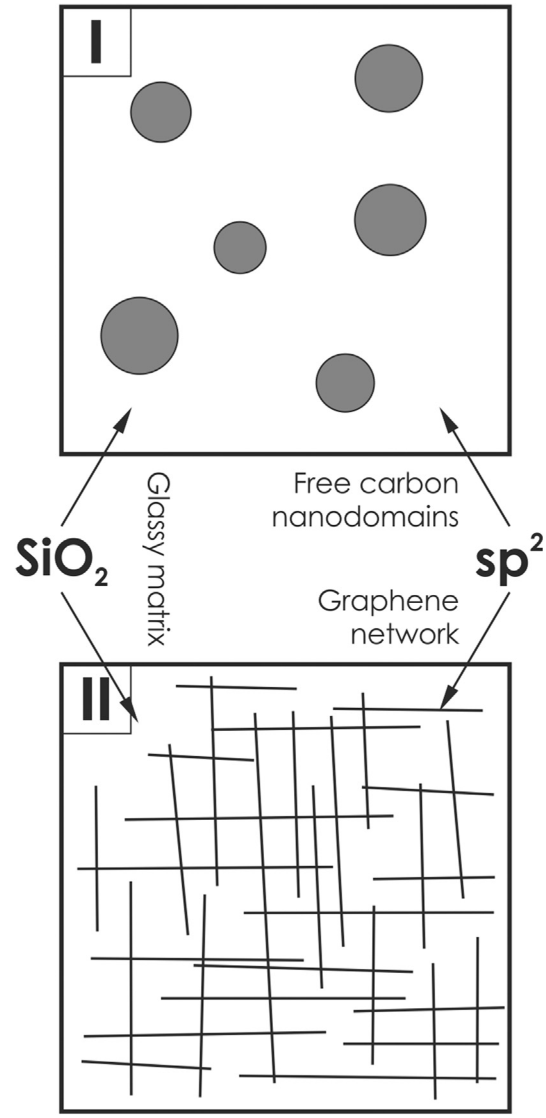

Fig. 1 – Structure of black glasses according to I) classic theory, II) alternative theory [15].

Thanks to these properties, these materials may find their application as protective-conducting coatings for chosen elements in Solid Oxide Fuel Cells. Use of ladder-like polysilsesquioxanes as a precursors, obtained by the sol-gel method, allow precise control of the ratio of carbon introduced into the structure and forming the free phase [13,17,18]. Thanks to this, it is possible to balance the mechanical, anticorrosive and electrical properties, providing a suitable material for SOFC application.

The main aim of this study was to evaluate possibility of using black glasses in the form of protective-conducting coatings on metallic interconnects in order to increase their corrosion resistance and preserve the favorable electrical properties of the metallic substrate.

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